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Safety Aspects of Oxygen Aeration Activated Sludge Systems

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This project was carried out to assess the impact of the use of oxygen and oxygen-enriched air for aeration of activated sludge systems on the safety of municipal wastewater treatment plants and their personnel. The tasks included (1) determination of oxygen combustion hazards from desk top analyses and smallscale flammability tests, (2) characterization and safety evaluation of oxygen aeration activated sludge systems from field visits and literature, (3) development of safety strategy and economics, and (4) preparation of standard safety manual and safety checklists for wastewater treatment with oxygen aeration.

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

The purpose of this manual is to provide guidance in the design and operation of wastewater treatment plants, using pure oxygen gas for aeration of activated sludge systems, so as to ensure the safety of treatment plant personnel and equipment.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

ABSTRACT

This project was carried out to assess the impact of the use of oxygen and oxygen-enriched air for aeration of activated sludge systems on the safety of municipal wastewater treatment plants and their personnel. The tasks included (1) determination of oxygen combustion hazards from desk top analyses and small-scale flammability tests, (2) characterization and safety evaluation of oxygen aeration activated sludge systems from field visits and literature, (3) development of safety strategy and economics, and (4) preparation of standard safety manual and safety check-lists for wastewater treatment with oxygen aeration. This manual appears separately as an EPA Report. The approach taken to this safety problem considers all potential sources of combustible and otherwise hazardous materials. This leads to the inclusion in the safety system of the wastewater train from collection through the secondary settler, and the oxygen train from on-site generation or trucked-in supply through the activated sludge reactor. The safety manual addresses itself to safe design and operation in all parts of this total system.

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SAFETY ASPECTS OF OXYGEN AERATION ACTIVATED SLUDGE SYSTEMS

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Safety concepts and details were discussed with oxygen aeration process developers. Those who took part in these discussions included: Charles Baker, Roger Carlson, Dr. L. Charles Matsch and Tom Walder at Linde Division of Union Carbide; Charles Block, Dr. Abraham Lapin, and Dr. Curt McDowell at Air Products and Chemicals, Inc.; Warren Francis and Dr. Bradley S. Kirk at Airco; and Richard B. Weber at FMC. In addition, safety discussions were held with Robert Lenhard at the Compressed Gas Association, and Vincent Grippi at Alexander Potter and Associates, both in New York, NY.

The interest of the EPA in this project was much appreciated. Helpful advice was received from Dr. Alfred A. Bacher, James Basilico, and Richard C. Brenner. Last, but not least, the encouragement and guidance of the Project Officer, Mr. Walter F. McMichael, must be acknowledged.

CONCLUSIONS

1. In view of the inherently greater hazard with oxygen, instead of air, aeration of activated sludge reactors, a valid safety approach must consider all potential external and internal sources of hazardous materials which can reach the reactor via the wastewater train, starting with the collection system.

2. By reason of their vicinity to the activated sludge reactor, any on-site oxygen generation and storage facilities must also be included in a total safety program.

3. From the standpoint of flammability and toxicity of the atmosphere over the liquid, open activated sludge reactor tanks are by their nature less hazardous than closed tanks. If, however, the concentration, flammability, volatility and solubility of hazardous substances in the wastewater are known, their hazard, if any, in closed tanks can be predetermined by calculating whether or not a flammable mixture exists in the tank freeboard gas phase. Generally, tanks located within buildings require more safety features than those in the open. Personnel hazards to be countered include falling into open tanks and off the top of closed tanks.

4. The flammability test apparatus constructed to obtain data not in the literature for a typical solvent and for hydrocarbon blends gave replicable data in all cases. Tested were dry and water vapor-saturated mixtures with oxygen, the latter simulating conditions under the cover of a closed oxygen aeration activated sludge tank. It was found that the presence of water vapor had no significant effect on the lean flammability limit (LEL). For a single gasoline sample the LEL decreased with time, evidence that volatiles were continuing to come off. This behavior, typical of blends, must be taken into account in safety monitoring. The apparatus is suitable for finding LEL's of combustibles in general.

5. Operating treatment plants with oxygen-aeration activated sludge systems were found to have specific safety monitoring and alarm features for the most part only in the oxygen supply and diffusion equipment, principally because these features were part of the equipment when installed.

6. Although to our knowledge no serious incident has occurred due to the use of oxygen aeration, the absence of a comprehensive plant-wide safety program can lead to serious incidents, in part because of a lack of knowledge of the presence of dangerous substances or conditions in the plant, and the hazards associated with them. Any unsafe conditions are aggravated by the presence and use of oxygen in the plant.

7. Process sensing instrumentation can frequently be made to do double duty as safety sensing instrumentation. Since safety is an axiomatic requirement, it cannot be expressed in terms of the usual process economics. Existing plants, depending on their current safety level, need to make additions of differing amounts. In new plants which include adequate safety devices and measures, the capital and O&M costs of the latter are of the order of $100,000.

8. There is a need for an overall safety program - involving sensors, alarms and associated personnel training - in oxygen aeration plants beyond the level of non-oxygen plants.

9. Most of the conditions desirable from a safety standpoint result in a better overall plant efficiency (e.g., a higher grade secondary effluent at lower cost) - improved safety means improved operation, and vice versa.

RECOMMENDATIONS

1. The Safety Manual for Wastewater Treatment with Oxygen Aeration prepared under this contract should be disseminated by the EPA to personnel associated with design and operation of existing and planned oxygen aeration plants.

2. The Manual should form the basis for a comprehensive safety training course for plant operators, with complementary audio visual material. This course should be required for all present and future operators in oxygen aeration treatment plants.

3. The Manual should be used as a general guideline for evaluation of safety features in commercial equipment for treatment plants employing oxygen.

4. Applicable portions of this Safety Manual should be incorporated into currently required operating manual and instructional program required by federal and state wastewater plant construction grant laws (e.g., PL 660).

5. The Clean Water Grant Program under PL 660 and similar state programs should be amended to include a category for oxygen aeration plants in levels of competence for operation of treatment facilities. This category might be akin to that required for operators of tertiary treatment plants, and include a training requirement which would include the safety course mentioned in 2. above.

6. The existing Manual should be expanded to include a section on specific hazardous materials which have a probability of occurring in industrial discharges or accidental spills. This section should contain graphs and charts for the rapid determination of the existence of hazards in the case of such discharges and spills.

7. Continuing efforts should be expended to improve the reliability, accuracy, ruggedness, etc., of devices which sense oxygen and hazardous substances (e.g., hydrocarbons, hydrogen sulfide, solvents, etc.) in the liquid and gas phases.

8. Probes which sense the concentration of hydrocarbons and other organics in the gas phase, generally are numerically accurate for only one specific compound, e.g., if calibrated for methane will not be accurate for propane or heptane, and still less so for hydrocarbon blends, etc. A probe should be developed to sense the degree of flammability of the gas mixture it samples, i.e., in effect to carry out automated mini-flammability tests with different amounts of oxygen addition. Such a device would be independent of the actual compounds present.

INTRODUCTION

ACTIVATED SLUDGE SYSTEMS WITH OXYGEN

Since its origin some 60 years ago by Ardern and Lockett (Ref. 1), the activated sludge process for the treatment of wastewater has become the predominant method for removal of organic matter. The principal reason for the widespread use of the activated sludge process is the rapidity with which the organic load is decreased when compared with early treatment methods such as lagooning. In addition, as the quantity of wastewater to be treated increased, both economic and esthetic considerations dictated utilization of the more efficient processing method.

Basically, the activated sludge process consists of contacting the wastewater with air to maintain a high-dissolved oxygen (DO) level necessary for the native microorganisms to metabolize the soluble organic load thereby converting dissolved organics to insoluble bacteria and other organisms. The mass of these organisms is called "activated sludge". Air is added to the system to agitate or mix the contents of the tank and to keep the system aerobic (containing uncombined oxygen) as demanded by the organisms.

During the course of evolution of the activated sludge process, numerous improvements in equipment were made directed at increasing both the efficiency and rate of transfer of oxygen from the gaseous to the aqueous phase. In the continuing search for process improvement, Okun (Ref. 2), some 25 years ago, initiated the first work using pure oxygen in lieu of air in a biological treatment process. He observed a decreased sludge volume compared with that found when air was used, and postulated that economics resulting from reduction of reactor volume would offset the higher cost of oxygen relative to air. Subsequent pilot plant studies (Ref. 3) confirmed the reduced sludge volume but indicated it was not sufficient to make the process as practiced economically attractive. Since that time, however, the economics of high purity oxygen have become more favorable due to advances in production technology.

A multiplicity of advantages of oxygen aeration over air aeration has been set forth (Ref. 4) dependent on the discovery of an efficient means of oxygen utilization. In the late 1960's a pilot plant study in closed reactor tanks conducted by the Linde Division of Union Carbide (Refs. 5 and 6) resulted in the UNOX process which provided high oxygen utilization. Other processes employing oxygen or oxygen-enriched air aeration with activated sludge, in both closed and open tank reactors, have been proposed and are in various stages of development. An overview of the use of oxygen in biological wastewater treatment through 1971 is given in Ref. 7 which contains a full bibliography. The EPA (and its predecessors) supported research and development of several of these processes to the tune of over $3 million by 30 June 1973, according to Ref. 8 which presents technical progress on EPA-supported projects during 1968 through 1973.

At this writing the process developers (in alphabetical order) and their processes are as follows:

Process Developer	Name of Process	Type of Reactor
Air Reduction Company (Airco)	F^3O	Open Tank
Air Products & Chemicals	OASES	Closed Tank, Multi-Stage
Chemetron	(prospective)	
Cosmodyne	SIMPLOX	Closed Tank, Single-Stage
Food Machinery & Chemical (FMC)	MAROX	Open Tank
Union Carbide, Linde Division	UNOX	Closed Tank, Multi-Stage

According to Ref. 9 which quoted statements of the developers as of July 1974, there were then 16 UNOX systems operating in the U.S.; OASES had 2, with 3 more under contract; MAROX was used in one treatment plant; and F^3O was to start up in one plant later in 1974. Some of the UNOX and SIMPLOX systems which were run in EPA demonstration projects (Ref. 8) are no longer in operation.

SAFETY IN WASTEWATER TREATMENT PLANTS

The safety record of American industry leaves much to be desired. Data for 1972 from OSHA (Ref. 10) disclose that 14,000 Americans get killed on the job annually, and 100,000 die every year from occupational diseases. Job-related injuries affect 5.7 million workers annually, and 300,000 are permanently disabled every year.

The Water Pollution Control Federation (WPCF) has been surveying safety in wastewater collection systems, and separately in treatment systems. The 1971 survey for wastewater treatment systems (pre-oxygen!) (Ref. 11) yielded the following facts:

1. The 771 plants which responded represented 45% of the sewered population of the U.S. and 25% of all treatment agency employees in the U.S.
2. The injury frequency rate of 37.3 per million man-hours worked was the highest for all industries, compared to a national all-industry average of 9.4 (National Safety Council).
3. 70% of the reporting plants reported no injuries, and 14% only one injury.
4. Large systems (those serving a population of more than 100,000) had a higher injury frequency rate than smaller ones.
5. 81% of the injuries occurred in 14% of the systems.

These figures indicate the existence of a large number of good safety programs, but also the need for more good programs, especially in the large systems. This has implications for oxygen, because the latter is destined primarily for large plants.

When oxygen is used on a large scale in wastewater treatment plants, there are additional potential hazards associated with (1) the oxygen generation and/or supply system, and (2) the activated sludge tanks in which oxygen, rather than air, reacts with the primary effluent. Since oxygen reacts more vigorously (compared to air) with organic matter, the latter must be excluded from atmospheres rich in oxygen. The history of development of cryogenic air separation plants to produce oxygen illustrates this

fact. These plants did not become routinely safe until continuous monitoring for possible organic contaminants, such as acetylene naturally present in air, and proper selection of materials and lubricants for oxygen service were instituted. Today, oxygen is handled routinely on a large scale in steelmaking, rocketry, and chemical processing. With proper precautions the use of oxygen in activated sludge sustems should also become routinely safe.

OBJECTIVES

The present program was carried out to assess the impact of the use of oxygen or oxygen-enriched air for aeration of activated sludge systems on the safety of municipal wastewater treatment plants and their personnel.

The purpose of this program was twofold:

(a) To evaluate the fundamental ramifications and implications from a safety standpoint of using oxygen gas or oxygen enriched air for aeration of activated sludge systems and, based on this evaluation, to recommend a course of action and master strategy plan for safety implementing oxygen technology in full-scale treatment facilities and ensuring the security and safety of treatment plant personnel and facilities.

(b) To develop a detailed standard safety manual and safety checklist for use by treatment plant designers and operators that identifies procedures, equipment, and instrumentation essential to the safe and proper handling of oxygen in a wastewater treatment plant environment and, further, that is sufficiently comprehensive and broad to apply to any rational oxygen dissolution concept.

APPROACH

In order to fulfill the stated objectives consideration was given to the place of the activated sludge system in relation to the wastewater treatment plant as a whole, and to the potential sources of hazardous materials which could be transported to the activated sludge system and there react with oxygen to endanger personnel and plant.

The extent of the system which needs to be considered from the standpoint of this safety study is shown on Fig. 1. The discussion is confined to municipal treatment plants accepting domestic and industrial wastes. On Fig. 1 the wastewater flows horizontally and the oxygen vertically - their confluence is the activated sludge reactor. The potential sources of hazardous materials which could lead to fires, explosions or toxicity are to be found throughout the treatment plant which includes on-site oxygen supply facilities, plus the collection system which feeds the plant. The collection system receives any externally generated hazardous matter which is discharged along with normal domestic and industrial wastewaters. In addition, such matter may be generated internally in the collection system and upstream components of the treatment plant through improper operating conditions.

Any equipment in which liquid or gaseous oxygen is flowing may become a source of hazard should external organic matter come in contact with the oxygen. Thus, on-site oxygen facilities must be included in a safety study. Such facilities consist at a minimum of a liquid oxygen storage system with a vaporizer, if liquid oxygen is trucked in. Alternatively, an on-site cryogenic air separation plant may produce liquid oxygen, or a molecular sieve absorbent air separation plan may produce gaseous oxygen.

In light of the above considerations and the axiom that an ounce of prevention outweighs a pound of cure, it is clearly insufficient to confine attention to the activated sludge reactor and equip it with elaborate "cure" features to try to deal with any hazardous material that may be coming down the pike at short notice. Rather, the approach taken is to examine

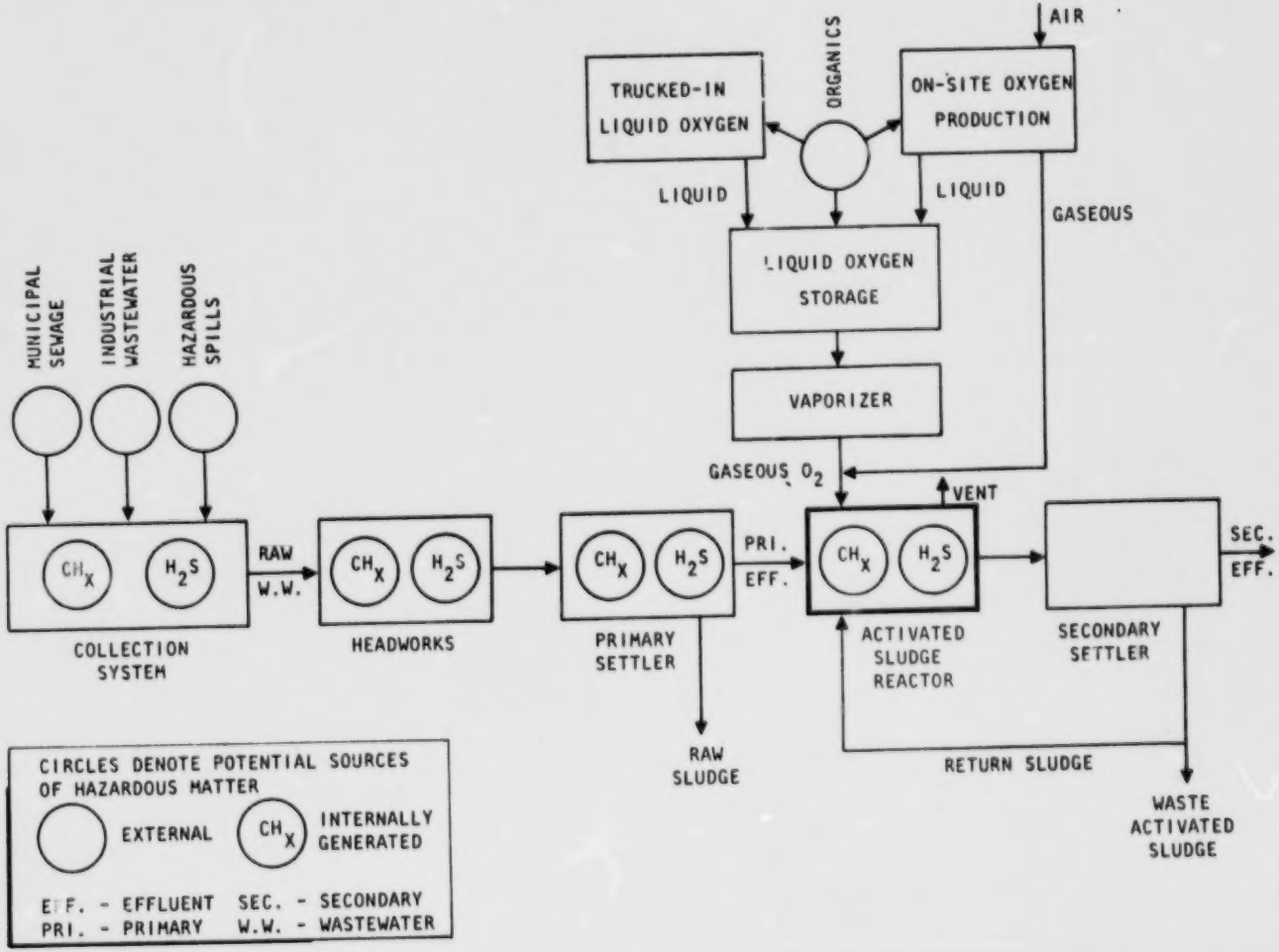

Figure 1. Total System for Oxygen Aeration Activated Sludge Safety Study

all sources of potential hazard upstream of the activated sludge reactor and devise preventive measures at every turn.

The first implication of this approach is that collection, treatment and oxygen systems must be considered together from the safety standpoint. If there are different jurisdictions for the different systems, means must be found at the human level to coordinate and collaborate in safety matters. Accordingly, the Safety Manual which is the end result of this study contains material on all three major systems. This is in line with the requirement stated in the previous Section that the Manual be "sufficiently comprehensive and broad to apply to any rational oxygen dissolution concept".

The approach to the manual includes two other major features which influenced the course of the study toward the objectives. The first is that the safety aspects outweigh all other considerations. It is obvious that in any process system (collection, treatment, oxygen supply) safe conditions are created through proper design followed by proper operation. Good design and good operation, both directed toward a high-grade product, already eliminate many safety hazards. Where there was a direct connection between design, operation and safety - and this was frequent - this was included in the Safety Manual. But the latter is in no way to be construed as a design or operating manual which must be specific to the particular plant and equipment. In contrast, the Safety Manual was written as a broader, encompassing document applicable to a variety of equipment, containing guidelines which specific plant manuals should incorporate in their more detailed treatment.

The second feature was that the manual be useful for plant design, plant operation and training of operators. This means that it be readable and easily comprehended by personnel of varied educational and experience backgrounds. Every effort was made toward thoroughness where needed, but with conciseness and organization for ready reference. No references to commercial process equipment or instrumentation are made in the Safety Manual. In the oxygen aeration activated sluge reactor field a multiplicity of process and instrumentation approaches are in development,

and no standard equipment or instruments exist at this time. Instead, different process equipment is identified by description of the different technical features, and instrumentation by the property to be measured, with required range and accuracy, where indicated for safety reasons.

Having set forth the major features of the approach to the safety study and Safety Manual, the more detailed activities in fulfillment of the objectives were delineated. These fell into the following major categories:

A. Determination of oxygen combustion hazards in the activated sludge application from desktop analyses and small-scale flammability tests, considering various combustible materials found in wastewater;
B. Characterization and safety evaluation of oxygen aeration activated sludge systems from field visits and literature;
C. Development of safety strategy and economics of safety in plants; and
D. Preparation of standard safety manual, including safety checklists.

The following Sections are devoted to these major categories. The Section on the preparation of the safety manual is a guide to the manual proper which appears in separate covers as an EPA Report.

OXYGEN COMBUSTION HAZARDS

Evaluation of the combustion or explosion hazard in oxygen aeration activated sludge reactors requires examination of the oxygen-wastewater system with regard to the simultaneous presence of (1) oxidizing materials, (2) fuel or combustible materials, and (3) ignition sources. For an incisive discussion of this problem, McKinley (Ref. 12) may be quoted verbatim:

"The oxygen-wastewater system has the following significant elements

a. the gas phase: the gas phase is at atmospheric pressure and consists of oxygen mixed with carbon dioxide, nitrogen, water vapor, and traces of other gases.

b. the liquid phase: the liquid phase is primarily water containing a suspension of microorganisms the concentration of microorganisms typically ranging from 1/3 to 3/4 weight percent.

c. the walls: the basin covers and walls are in contact with liquid or gas and provide a surface on which biological floc, grease or other solid matter may buildup.

d. the machinery: this portion of the system consists of all the moving parts, such as aerators, bearings, recycle pumps (and compressors).

e. the oxygen supply system.

f. the people.

It is the interaction of all these system elements which must be examined in an analysis of any potential oxygen enriched atmosphere hazard.

As we methodically proceed with the hazards evaluation for a system, looking for fuel and ignition sources, we will do so with a variety of very practically oriented questions in mind, such as:

1. If a localized fire starts will it spread or will it go out?
2. Is sufficient fuel present to cause a problem if it completely burns?
3. Is there any way for an explosion to occur?
4. Is it possible for a soluble liquid or gas to enter the system with the wastewater feed and become concentrated inside the system to a concentration level which would be hazardous?
5. Can floating solid or liquid fuels enter the system and become a problem at the liquid-gas interface?

The classical oxygen-fuel-diluent triangle provides understanding of the oxygen enriched atmosphere hazards relative to the oxygen activated sludge operation (Figure 2). Each corner represents 100% concentration of the component: oxygen, or fuel, or diluent. In a practical and complex system, such as in our case, the fuel may be a mixture and several diluents may be involved. By adding the behavior of these together we may make a simplified representation to show whether the system is in a safe region of operation as indicated by area B or in an unsafe area, as indicated by area A. Our safety objective must, of course, be to understand our system sufficiently well that essentially all parts of it are always operating in area B and not in area A. In area B, even if ignition energy is supplied the flame cannot propagate - it will die out. In area A flame propagation will occur - explosive energy release may result."

For any potentially explosive mixture, a combustible-lean limit and a combustible-rich limit exist, referred to as the lower explosion (or flammability) limit (LEL) and the upper explosion (or flammability) limit (UEL). A numerical example for the methane/oxygen/nitrogen system is shown in Figure 3, taken from Ref. 13, based on References 14 and 15. From this, it is seen that for the methane/oxygen system LEL = 5.1% methane, and UEL = 61% methane. At the nitrogen diluent concentration of 21% the air composition is reached, for which LEL = 5% methane and UEL = 15% methane. Now in the oxygen aeration activation sludge system it is the LEL which is the characteristic of interest. Figure 3 and Table 1 indicate that LEL values are fairly constant regardless of the

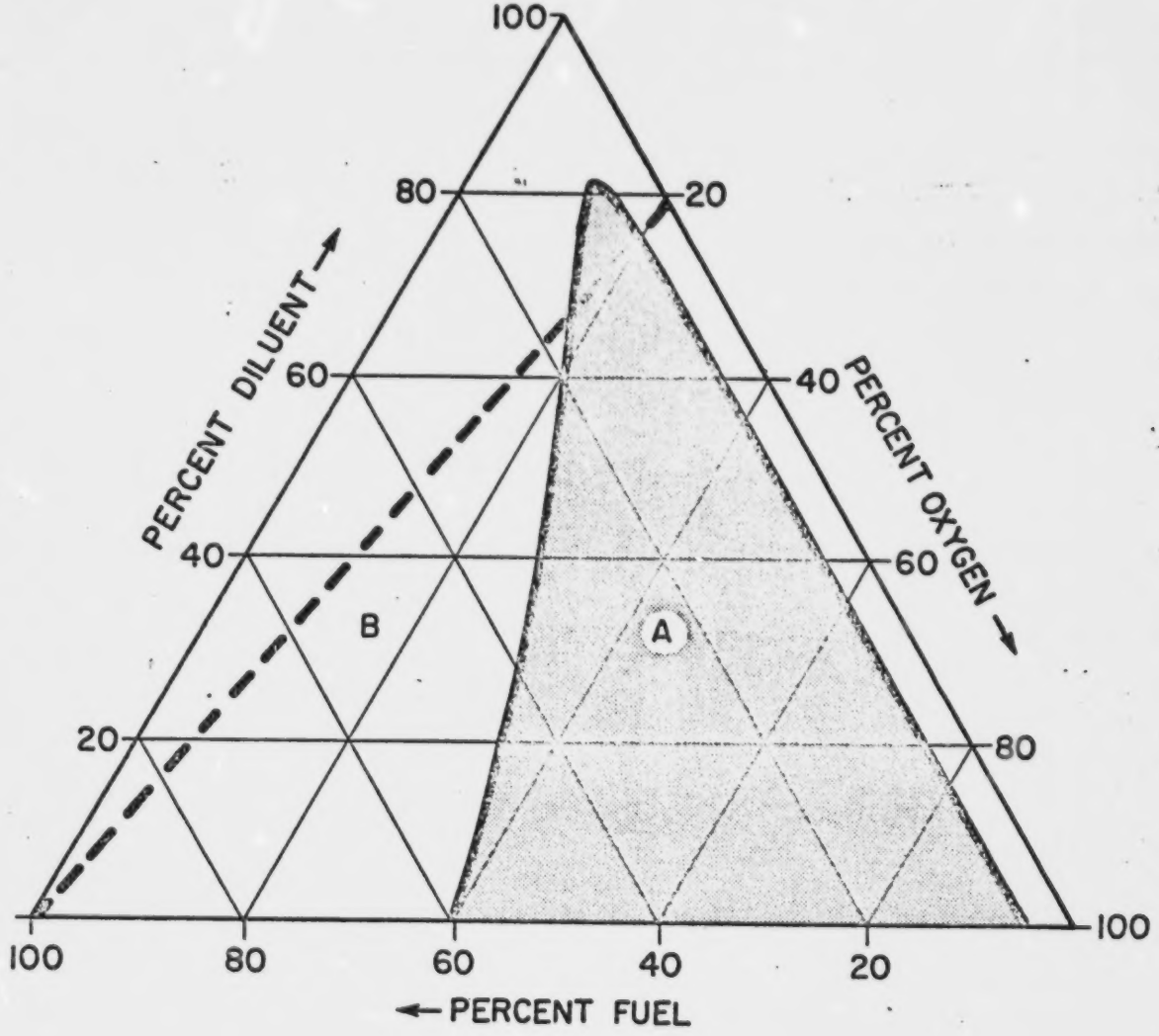

Figure 2. Classical Oxygen-Fuel-Diluent Composition Diagram (from Ref. 12)

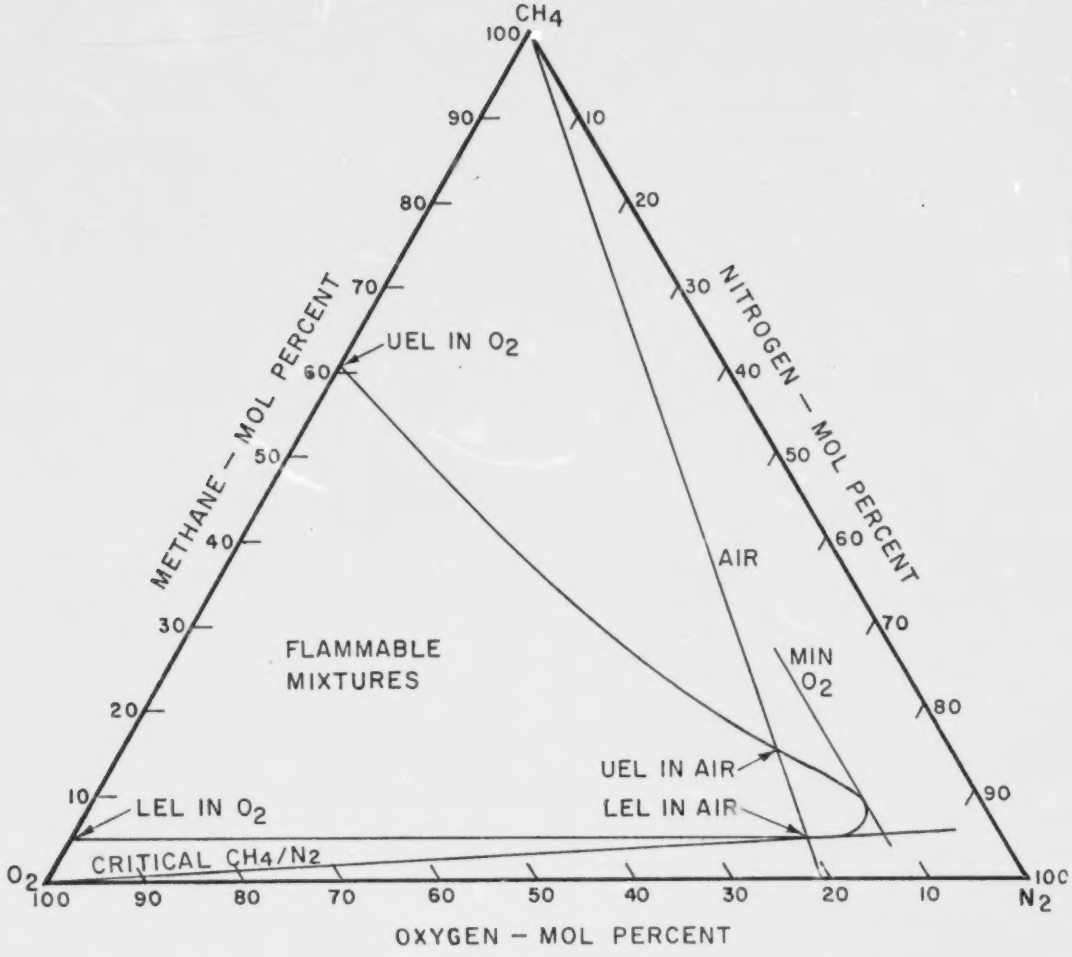

Figure 3. Flammability Diagram for $CH_4/O_2/N_2$ System
(From Ref. 13, 14, and 15)

Table 1. LOWER LIMITS OF FLAMMABILITY (LEL) OF FUEL GASES AND VAPORS WITH OXYGEN AND WITH AIR (PERCENT FUEL BY VOLUME) (Ref. 14)

Compound	Formula	Pure Oxygen	Atmospheric Air
Hydrogen	H_2	4.0	4.0
Carbon Monoxide	CO	15.5	12.5*
Ammonia	NH_3	15.0	15.0
Methane	CH_4	5.1	5.3
Ethane	C_2H_6	3.0	3.0
Ethylene	C_2H_4	3.0	3.1
Propylene	C_3H_6	2.1	2.4
Cyclopropane	C_3H_6	2.5	2.4
Diethyl ether	$C_4H_{10}O$	2.0	1.9
Divinyl ether	C_4H_6O	1.8	1.7

amount of diluent added, and that, in particular, LEL values in air and oxygen are very close. (Figure 3 shows that this is not true for UEL values.) Table 2 shows additional flammability limits as well as minimum oxygen concentrations for universal flammability (see Figure 2), computed by Baker and Carlson (Ref. 13).

When flammable mixtures are formed by accident, it is usually desirable to reduce the combustible concentration quickly by adding enough air or inert gas to lean out the mixtures into the non-flammable region. The addition of increasing amounts of a chemically inert substance to the mixtures causes the lean and rich limits to approach each other and ultimately meet. A comprehensive study of the effect of several diluents (carbon tetrachloride, carbon dioxide, nitrogen, helium and argon) on methane limits in air is described by Coward and Jones (Ref. 14). The extinctive efficacies of the diluents in decreasing order are

$$CCl_4 > CO_2 > N_2 > He > A.$$

The experiments producing these results were carried out in tubes of 5 cm diameter. In tubes of smaller diameter, helium increases in efficacy due to its very high thermal conductivity, otherwise the effects correspond closely to the specific heats of the diluents. For tests in air with JP-4, a distillate fuel, and nitrogen and carbon dioxide diluents at 70 F at various pressures, Stewart and Starkman (Ref. 16) report that there is little or no difference between these inertants in their effect on the lean limit.

In regard to mixtures of several flammable gases and vapors, a simple formula, of additive-character, was advanced by Le Chatelier (Ref. 17) to connect the lower limits of two gases with the lower limit of any mixture of them. It is

$$\frac{n_1}{N_1} + \frac{n_2}{N_2} = 1,$$

in which N_1 and N_2 are the lower limits (volume percent) in air for each combustible gas separately, and n_1 and n_2 are the percentages of each gas in any lower limit mixture of the two in air.

Table 2. FLAMMABILITY LIMITS OF GASES IN OXYGEN OR AIR (from Ref. 13 based on Ref. 14)

Gas	Flammability Limit, % (* in air)		Oxygen % below which no mixture is flammable with air diluted by	
	Lower	Upper	N_2	CO_2
Hydrogen	4.0	94	5.0	5.9
Carbon Monoxide	15.5	94	5.6	5.9
Methane	5.1	61	12.1	14.6
Ethane	3.0	66	11.0	13.4
Propane	2.3	55	11.4	14.3
Butane	1.8	49	12.1	14.5
Isobutane	1.8	48	12.0	14.8
Pentane	1.5*	--	12.1	14.4
Hexane	1.2*	--	11.9	14.5
Heptane	1.2*	--	----	----
Octane	1.0*	--	----	----
Nonane	0.8*	--	----	----
Ethylene	3.0	80	10.0	11.7
Propylene	2.1	53	11.5	14.1
Butylene	2.0*	--	----	----
Acetylene	2.5*	--	----	----
Benzene	1.4*	--	11.2	13.9
Toluene	1.4*	--	----	----
Styrene	1.0*	--	----	----
Cyclopropane	2.5	60	11.7	13.9
Methanol	7.3*	--	10.3	13.5
Ethanol	4.3*	--	----	----
Ethyl Ether	2.0	82	----	----
Acetone	3.0*	--	13.5	15.6
Gasoline	1.4*	--	11.6	14.4
Kerosine	0.7*	--	----	----
Naphtha	0.8*	--	----	----

The formula indicates that, for example, a mixture of air, carbon monoxide and hydrogen, which contains one-quarter of the amount of carbon monoxide and three-quarters of the amount of hydrogen necessary to form a lower-limit mixture, will be a lower-limit mixture. If the formula is true, the lower limits of flammability form a series of flammability equivalents for the individual gases of a mixture. The formula also indicates that lower-limit mixtures, if mixed in any proportions, give rise to mixtures that are also at their lower limits. In Ref. 14 it is stated that the formula may be generalized to apply to any number of combustible gases, thus:

$$\frac{n_1}{N_1} + \frac{n_2}{N_2} + \frac{n_3}{N_3} + \ldots = 1,$$

which may be expressed as

$$L = \frac{100}{\frac{P_1}{N_1} + \frac{P_2}{N_2} + \frac{P_3}{N_3} + \ldots}$$

where L is the lower limit of the mixture of combustible gases and P_1, P_2, P_3 . . . are the proportions by volume of each combustible gas present in the original mixture, free from air and inert gases, so the

$$P_1 + P_2 + P_3 + \ldots = 100$$

For example, the lower limit of a "natural gas" of the composition

Subscript	Gas	P	N
1.	Methane	80	5.3
2.	Ethane	15	3.22
3.	Propane	4	2.37
4.	Butane	1	1.86
		100	

is given by

$$L = \frac{100}{\frac{80}{5.3} + \frac{15}{3.22} + \frac{4}{2.37} + \frac{1}{1.86}} = 4.55$$

In noting that the accuracy of the formula has been tested carefully for many mixtures, it is also stated in Ref. 14 that while, in general, the formula is often correct or very nearly so, there are some marked exceptions. Many of the discrepancies are found with upward-propagating flames, especially when one of the constituents is a vapor, such as ether or acetone, capable of giving rise to the phenomenon known as a "cool flame". Le Chatelier's law is useful when its applicability has been proved, but it should not be applied indiscriminately. The formula has been used to represent limits for various industrial gases for which experimental data are available. Hence, it is possible to find the minimum amount of a diluent and/or the maximum amount of oxygen for non-flammability of a given gas mixture.

When a combustible liquid is added to the wastewater stream, its solubility in water determines the concentration of its vapor in the gas phase above the liquid surface (freeboard). When the tank is closed at the top, it is possible to compute vapor equilibrium concentrations using solubility data and Henry's Law for dilute solutions. Generally, for hydrocarbons, solubility decreases with increasing molecular weight. Solubility is lowest for paraffins, increasing with olefins, aromatics and acetylenes, in that order. Solubilities and Henry's Law constants of different hydrocarbons (Ref. 18) are shown in Table 3, taken from Ref. 13.

The combined effect of concentration flammability, solubility, and volatility determines the combustion hazard of an ignitable substance. In Ref. 13 numerical computations are made to show that a given quantity of benzene (which is highly soluble) causes a vapor concentration much below the LEL, while the same amount of n-octane (which is less soluble) results in a vapor concentration nearly twice that of the LEL. Table 4, from Ref. 13, shows what size spills of selected infinitely soluble hydrocarbons are required to produce LEL mixtures. For more volatile substances, e.g., acetone, a smaller spill is shown to be flammable,

Table 3. SOLUBILITY OF HYDROCARBONS IN WATER (From Reference 18)

Hydrocarbon	Solubility Limit at 25°C, gm H/C per 10^6 gm water	Henry's Law Constant, psia per mole fraction
Methane	24.4 ± 1.0	537,000
Ethane	60.4 ± 1.3	406,000
Propane	62.4 ± 2.1	576,000
n-Butane	61.4 ± 2.6	772,000
Isobutane	48.9 ± 2.1	970,000
n-Pentane	38.5 ± 2.0	1,040,000
Isopentane	47.8 ± 1.6	1,006,000
n-Hexane	9.5 ± 1.3	1,430,000
2-Methylpentane	13.8 ± 0.9	1,420,000
3-Methylpentane	12.8 ± 0.6	1,380,000
2,2-Dimethylbutane	18.4 ± 1.3	1,600,000
n-Heptane	2.93 ± 0.20	1,650,000
n-Octane	0.66 ± 0.06	2,590,000
Ethylene	131 ± 10	175,000
Propylene	200 ± 27	172,000
1-Butene	222 ± 10	206,000
Propyne	3640 ± 125	8,990
Cyclopentane	156 ± 9	153,000
Cyclohexane	55 ± 2.3	168,000
Methylcyclohexane	14.0 ± 1.2	349,000
Benzene	1780 ± 45	4,580
Toluene	515 ± 17	5,560
o-Xylene	175 ± 8	4,310
Ethylbenzene	152 ± 8	7,130

Table 4. SPILLS OF INDUSTRIAL WASTE CHEMICALS TO PRODUCE FLAMMABLE MIXTURES (from Ref. 13)

Chemical	LEL Mole %	Liquid Concentration		Required Spill gal/MM gal. waste
		Mole Fraction	mg/l	
Acetone	2.6	0.012	36,000	48,000
Methanol	6.7	0.326	410,000	1,100,000
Ethanol	3.3	0.203	360,000	820,000
n-Propanol	2.2	0.779	750,000	14,600,000
n-Butanol	1.7	*	*	*

* cannot reach LEL until liquid is pure alcohol at 35°C

while for the less volatile alcohols extremely large spills would be necessary. This calculation method can be applied to treatment plant components upstream of the activated sludge reactor, such as the sewer or aerated grit chamber, to determine the actual gas mixture in the influent to the activated sludge reactor, with examples in Ref. 13.

FLAMMABILITY TESTS

In this study, it was desired to consider hydrocarbons, spent cleaning solvents, fuel oils, fats and greases as potentially combustible substances in the humid, oxygen-rich atmosphere in activated sludge tanks with oxygen aeration. The preceding account of the state-of-the-art in flammability permitted an analytical investigation of the effects of fuels, fats and greases. It was found that, *at room temperature*, which is of interest in the activated sludge application, the high molecular weights and low vapor pressures of these types of materials place their vapors in the region of non-ignition. Of course, these materials also have very low solubility so that they would float on the water surface. The practically infinite heat sink provided by the bulk water would be expected to preclude any ignition of the condensed phase, unless it be via a wicking material as in a candle, a most unlikely event.

Calculation methods exist for the estimation of flammability limits for mixtures of vapors and diluents, as previously outlined. However, the flammability of water-vapor-saturated oxygen-fuel gas mixtures does not seem to have been determined, and data on typical industrial volatile distillate fuels are not known. Therefore, it was decided to construct a flammability limit test apparatus and to measure the LEL in association with dry oxygen, and with oxygen in a water-saturated atmosphere of the following substances (details in Table 5):

- Methane (CH_4): to establish the validity of the apparatus
- Methyl ethyl ketone (C_4H_8O): a representative cleaning solvent
- Paint thinner: a hydrocarbon blend of low volatility
- Gasoline: a hydrocarbon blend of high volatility

Table 5. CHARACTERISTICS OF GASES AND LIQUIDS TESTED IN FLAMMABILITY TEST APPARATUS

Oxygen

Grade 4.5 (ultrapure, 99.995%), Airco

Methane

Grade 2 (purified, 99.0%), Airco

Molecular Wt. 16
Melting Pt. -182.5 C (-296 F)
Boiling Pt. -161.5 C (-259 F)
Solubility in water 0.0244 gm/liter at 25 C (77 F)

Methyl Ethyl Ketone

Practical Grade, Baker

Molecular Wt. 72
Density 20/4 .805
Melting Pt. -86.4 C (-124 F)
Boiling Pt. 79.6 C (175 F)
Solubility in water 35.3 gm/liter at 10 C (50 F)

Paint Thinner
AMSCO 20-H,
M-350-53

API Gravity	= 46.6
Flash Point, TCC	= 103 F
Koury-Butanol No	= 38
Aniline Point	= 142 F

Distillation:

IBP	= 312 F
50%	= 334 F
95%	= 364 F
EP	= 390 F

Composition:

Aromatics	3.5
Naphthenes	67.0
Paraffins	26.0
Other	3.5
	100.0

Gasoline, Low Lead
Standard Oil of CA
Transition Grade

API Gravity	= 58.0
Reid Vapor Pressure, 100 F	= 8.9 psia

Distillation:

IBP	= 95 F
50%	= 209 F
95%	= 315 F
EP	= 385 F

DESIGN OF TEST APPARATUS

In a typical flammability limit test, the gas mixture of interest is introduced into a tubular enclosure provided with a spark gap. If combustion and flame propagation occur when the spark is activated, the combustible concentration is considered to lie within the flammable limits. When a spark or other source of heat energy of sufficient size and intensity is introduced into a lean mixture, some combustion occurs even when the mixture concentration is below the lower flammability limit, i.e., incapable of flame propagation. Such local flames are extinguished when the influence of the ignition energy flow stops. The distinction between combustion and detonation should be noted. Quoting from Lewis and Von Elbe (Ref. 19): "A combustion wave propagates by the processes of heat transfer and diffusion, whereas a detonation wave is a shock wave which is sustained by the energy of the chemical reaction initiated by the temperature and pressure of the wave. Combustion waves are slow compared to the velocity of sound whereas detonation waves travel faster than sound. Generally, when an explosive mixture is weakened by dilution with an excess of either constituent or with inert gas, a *limit of detonability* is found, but mixtures outside the limit of detonability support combustion waves until the dilution has been carried further to the *limit of inflammability*."

A basic disagreement exists concerning the nature of flammability limits, i.e., are they fundamental physicochemical constants or strictly characteristics of the apparatus used? Coward and Jones (Ref. 20) defined the flammability limit in the following way: "A flammable mixture of gases such as methane and air may be diluted with one of its constituents or with other gases until it is no longer flammable. The dilution limit of flammability, or simply the limit of flammability, is the border-line composition; a slight change in one direction produces a flammable mixture, in the other direction a nonflammable mixture."

Gerstein and Stine (Ref. 21) say that although it is not often explicitly stated, it is assumed that the limit, so defined, is independent of the experimental apparatus and is, indeed, a dilution or concentration limit, a fundamental flammability limit, as opposed to a quenching distance or an apparent flammability limit associated with heat losses. Belles and Swett (Ref. 22) state that flammability limits "may be made independent of any apparatus effects; therefore, these limits are physicochemical constants for each fuel." Also, Berlad and Yang (Ref. 23) have implied that radiation loss produces a fundamental flammability limit.

However, more recent work by Gerstein and Stine (Ref. 21) has indicated that a fundamental flammability limit, independent of heat loss, does not exist even when radiation loss is considered. They have defined a region of diameters in which radiation loss exceeds conduction and, therefore, quenching is negligible. An "apparent flammability limit" can thus be obtained. Also, Mullins (Ref. 24) states that the "continued flame propagation depends on the nature of the apparatus containing the given mixture as well as other factors ... For these reasons, the limiting mixture compositions which are flammable cannot be regarded as absolute constants."

After a thorough study, Linnett and Simpson (Ref. 25) concluded that while fundamental limits may exist, there is no experimental evidence to indicate that such limits have been measured. Although Zabetakis also has concluded (Ref. 15) that "the limits of flammability obtained in an apparatus of suitable size and with a satisfactory ignition source should not be termed fundamental or absolute limits until the existence of such limits has been established," he notes that "as long as experimentally determined limits are obtained under conditions similar to those found in practice, they may be used to design installations that are safe and to assess potential gas-explosion hazards".

In light of the cited references and because propagation has been observed in mixtures beyond the published "limits", not only in the laboratory (Ref. 26), but also in industrial and mining explosions, flam-

mability measurements were planned under conditions which simulate oxygenation in activated sludge systems. This involved consideration of the following design factors;

1) *Direction of Flame Propagation*. Ranges of flammability are widest for upward propagation, narrowest for downward propagation, and intermediate for horizontal propagation. The lean limit does not appear to be greatly affected, however (Refs. 24 & 27).

2) *Vessel Diameter*. As a general rule, flammability ranges widen as the tube diameter is made larger, but the change for diameters above 5 cm in diameter is very small, rarely exceeding a few tenths of 1% (Ref. 24).

3) *Vessel Length*. Variation in length of the tube, provided it is long enough for the initial impulse of the source of ignition to be dissipated, has no effect on the limits of a tube open at one end (Refs. 20 & 24).

4) *Turbulence*. Although it is known that fuel-air mixtures can be circulated slowly through a tube by way of an external by-pass without appreciably affecting the flammability limits that are obtained for the same mixture contained statically in the tube (Ref. 28), work by other investigators on the effects of turbulence (Refs. 20 & 29) has shown a change in flammability limits.

5) *Temperature at Time of Ignition*. Temperature changes of a few degrees at the time of ignition have little effect on the limits. At temperatures considerably above room temperature, the limits are somewhat wider (Ref. 24 & 27).

6) *Pressure*. As with temperature, small pressure changes have a negligible effect on the explosion limits (Ref. 24).

7) *Humidity*. A normal amount of water vapor in the mixture prior to ignition seems to have no effect on the lower limit (Ref. 27), but it acts to lower the rich limit. Carbon monoxide is exceptional in that humidity markedly affects the lean limit (Ref. 24 and Table 1).

8) *Spark Ignition*. A flammable mixture may be ignited locally by use of a spark, and a flame front or combustion wave will propagate from the spark through the mixture somewhat in the manner of a light wave, that is, every point in the wavefront serves as an ignition source and the propagation of the wave conforms to Huygens' principle. Such a type of ignition, whether it be initiated by a spark or small flame has been described by Lewis and von Elbe (Ref. 19) as being generated by a point-like ignition source. For point electrodes, it is necessary (Ref. 24) to ensure that electrode spacing exceeds the quenching distance, i.e., the minimum electrode spacing below which the reaction initiated in a hydrocarbon-air mixture by an incendiary spark is quenched.

9) *Gas Delivery System*. The apparatus must be so designed that backflow and/or flame propagation upstream is precluded.

Decisions on these nine design factors were made, leading to the following concept, illustrated in Figure 4. An approximately three-foot long vertical combustion chamber fabricated from 2-inch (5 cm) diameter stainless steel tubing is loaded with gas-vapor mixtures in upward flow using a gas delivery system which includes K-bottles, regulators, rotameters, metering valves, shutoff valves, and a special low-volatile-compound holding vessel. The holding vessel and combustion chamber are isolated from the other equipment and the operator by a barricade. The contents of the chamber are monitored by various sensing devices through hookups located along the chamber. There are also provisions for sampling the gas mixture prior to ignition for gas chromatographic (g.c.) analysis. A spark ignition source provided near the bottom end of the vertical chamber is then activated. It has been noted (Ref. 15) that, in general, many flammable mixtures can be ignited by sparks having a

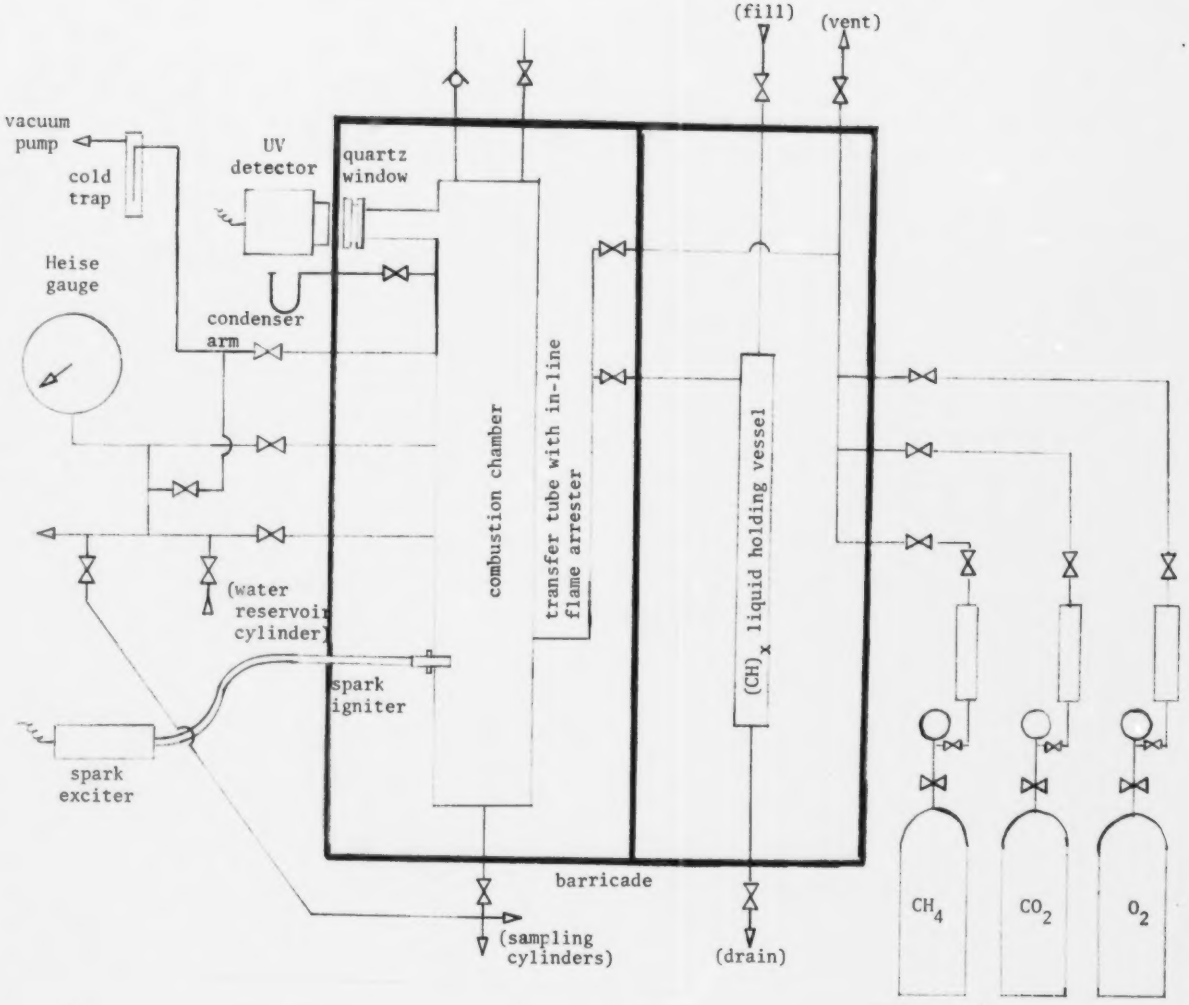

Figure 4. Schematic of Final Flammability Test Apparatus Configuration (Diagram - Not to scale - Instrumentation partially shown)

relatively small energy content (1 to 100 millijoules) but a large power density, in excess of 1 megawatt/cm^3. Therefore, a spark ignition source is used which meets or exceeds these requirements. Ensuing flame propagation to the opposite end of the chamber from the ignition source indicates that the particular gas mixture is within the flammability limits. The occurrence of flame propagation to the end of the chamber is determined automatically by a UV radiation sensor set up to view the chamber contents through a special quartz-window viewing-point assembly.

The actual laboratory flammability test apparatus is shown in the photograph in Fig. 5. The apparatus includes the combustion chamber, volatile-gas delivery manifold, low volatility liquid reservoir, spark ignition subsystem, flame detection subsystem, gas composition monitoring subsystem, and pressure/temperature monitoring subsystems. As can be seen in Fig. 5, most of the subsystems were installed in a fume hood equipped with a system mounting rack. The barricade panels for protection of personnel and equipment are shown in place. Of prime importance in the design was the elimination of hazards to both personnel and equipment. The combustion chamber, 42-inches long, visible in Fig. 6 (taken during the apparatus buildup stage), is made (as stated earlier) of 2-inch stainless steel tubing with a horizontal arm and flange for the quartz window. There are seven hookup locations along the tube, five for gas lines and two for a choice of spark igniter positions. Both ends of the combustion tube have been flared for AN plugs, which have been machined for several additional plumbing connections. A 3/4-inch check valve with a low cracking pressure (8-inches H_2O, max.) and a high Cv factor (17.7) can be seen attached to the top plug for automatically venting the product gases subsequent to combustion. In addition, a tape heater has been would around the base of the combustion chamber so that temperature gradients with their resultant gas convection currents can be established in the chamber to mix the gases.

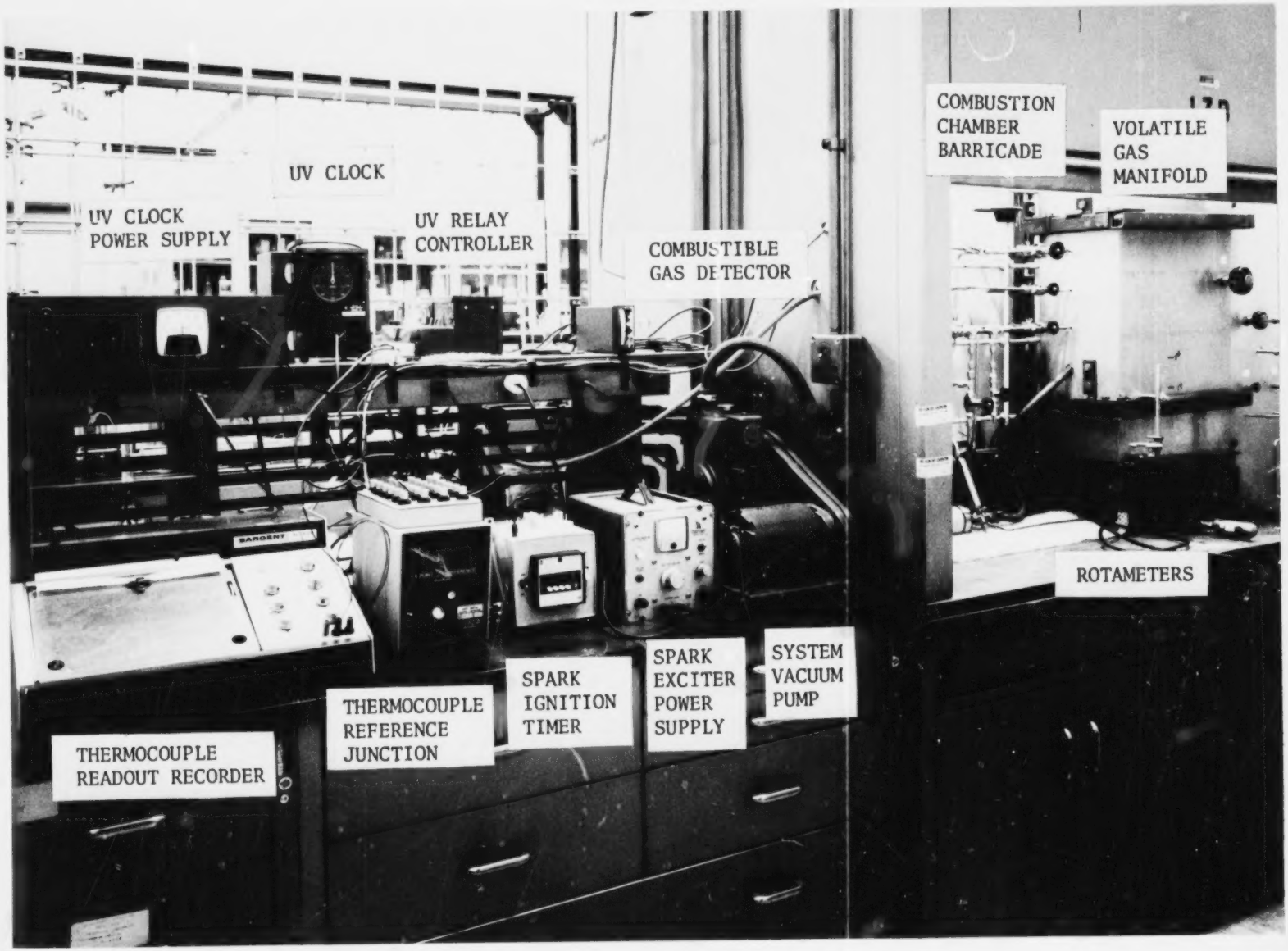

Figure 5. Overall View of Flammability Test Apparatus

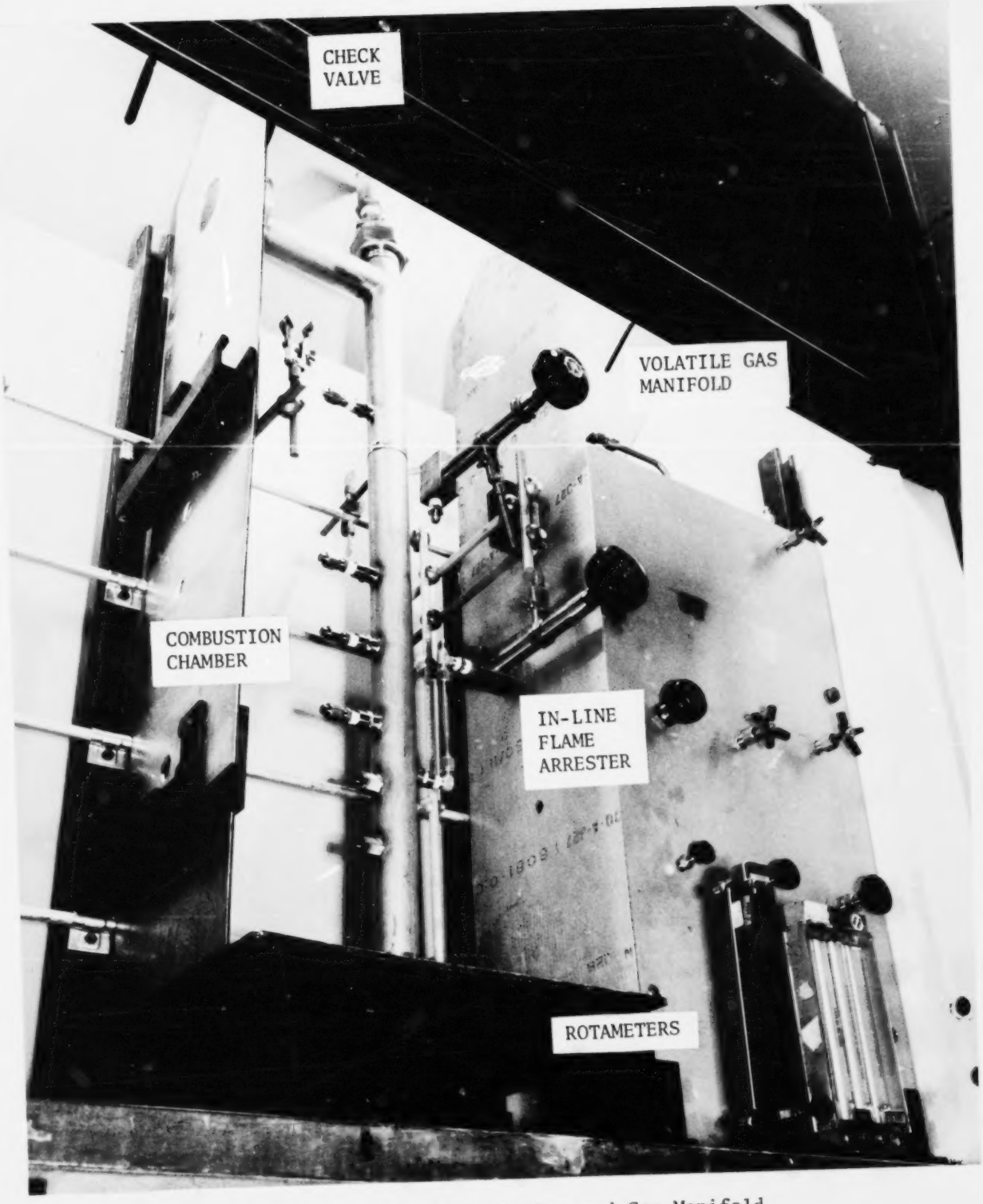

Figure 6. Combustion Chamber and Gas Manifold

The volatile-gas delivery manifold was panel-mounted behind a metal barricade located to the right in the fume-hood, seen in Fig. 5. It consists of three shutoff valves, three metering valves, a vent valve, and interconnecting 3/8-inch stainless steel tubing for delivering oxygen, methane, and inert gas to the combustion chamber in measured quantities. The combustion chamber and gas delivery manifold were assembled and helium leak-tested as separate subsystems and then combined into an integrated system and leak-tested again. All vacuum leaks were located and successfully eliminated using this procedure. The transfer tube connecting the two subsystems contains an in-line flame arrester consisting of a 4-inch length of 3/8-inch stainless steel tubing packed with 1/8-inch stainless steel balls held in place by stainless steel screens. Both subsystems are located behind the metal barricade, which also separates them from each other. The compressed gas cylinders are located to the right of the fume hood, and the gas delivery lines run into the fume hood to a set of rotameters which are connected to the gas delivery manifold. For ease of access, the rotameters were not housed in the manifold panel, but were installed in front of the barricade.

The liquid reservoir for combustible vapors of low volatility is connected to the combustion chamber and is located behind the protective barricade for the volatile-gas delivery manifold as depicted in Fig. 4. The reservoir was designed to be cleaned out and loaded in situ. It consists mainly of stainless steel tubing and components assembled in such a manner that a sample is drawn from the vapor phase, which, in the case of a fuel blend, would be representative of the vapor from a large spill. In normal usage, the reservoir is evacuated, loaded with a quantity of the appropriate liquid fuel, and opened slightly to the evacuated combustion chamber several times to remove the previously dissolved inert gases. The combustible gas vapor is then bled into the combustion chamber until the desired pressure, which is approximately that which would give an LEL mixture with one atmosphere of oxygen, is attained.

In the search for an adequate spark ignition source, many devices were eliminated because they could not meet the basic energy (1-100 mj), power density (1 megawatt per cubic centimeter), and spark rate (40 sparks per second) requirements. The spark rate requirement was imposed due to studies reported by Laffitte and Delbourgo (Ref. 30), which showed that somewhat lower values for lean flammability limits are obtained with multispark ignition sources as opposed to single-spark systems. Most inductive discharge units fulfill the energy requirement, but because of the spark pulse time (1-5 millisecond) are not able to meet the required power density level. Capacitative discharge units, however, are capable of meeting both the energy and power density requirements (their pulse time is generally less than 50 microseconds/spark), and some are available with the desired spark rate. A suitable unit was obtained from an in-house source. It consists of an ignition exciter (Fig. 7), a mating igniter with a 0.050-inch radial surface gap, an ATC solid state timer (Fig. 5), a "slave" relay, a DC power supply (Fig. 5), and associated power switches. The exciter produces a spark pulse of 90 millijoules for 30 microseconds duration at a measured spark rate of 57 sparks/second. With the integration of the solid state timer into the circuit, the ignition subsystem can be preprogrammed to spark for a specified period of time. This feature is useful for determining the effect of varying ignition times on the lower flammability limit and can be employed to prevent any interaction between the ignition spark and the UV flame detector.

INSTRUMENTATION AND TEST PROCEDURES

Considerable attention was given to the ultraviolet (UV) flame detector system. Many devices were eliminated because they could not meet the basic requirement of essentially instantaneous response. This requirement results from the exposure of only about two inches of combustion chamber vertical height to the cone of vision of a UV detector through the quartz-window viewing port. If the flame speed were 200 inches per second (a representative value with oxygen), the detector system would

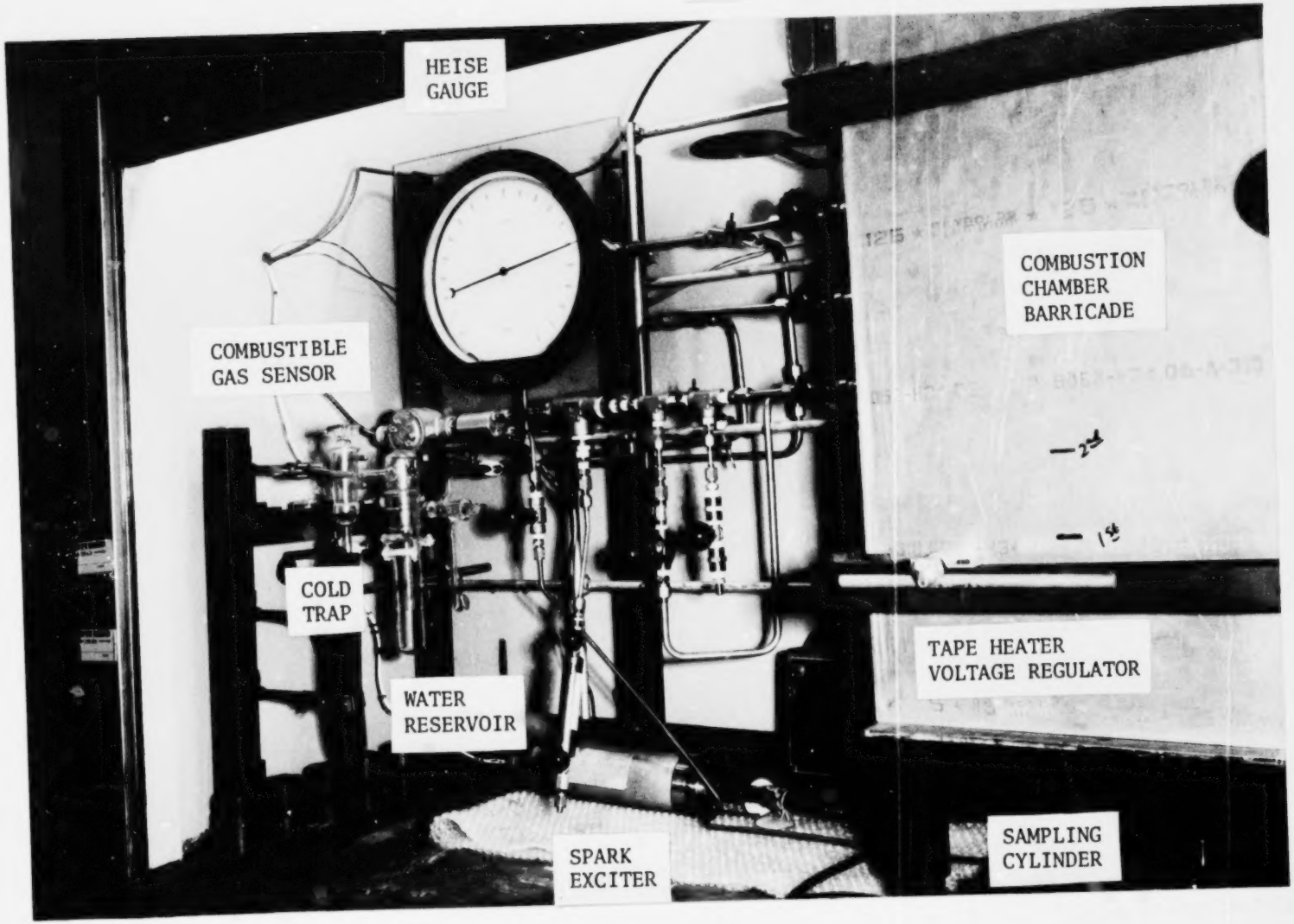

Figure 7. Gas Sampling System

have only 10 milliseconds of viewing time in which to trigger a response or signal. The detector response time must be less than the time for viewing the flame front. Therefore, a UV flame detection system with a response time of a few milliseconds was ordered as a special unit from Detector Electronics, Minneapolis, Minnesota. The special system includes a solid state relay, a high speed gold cathode tube module, and a special sensitivity-setting circuit board, all designed to reduce the detector response time below the typical response time to an intense UV source of 25 milliseconds for a standard unit.

To increase the residence time of a flame front in the field of vision of the detector, the stainless steel view tube which houses the viewing port was made 2-inches in diameter and 6 inches long. The dimensions of the horizontal view tube will permit a flame front in a combustible gas mixture to propagate through the view tube towards the UV detector thereby increasing the flame front residence time in the detector cone of vision. As shown by Linnett and Simpson (Ref. 25), a flame front of a lean limit mixture travelling upward in the vertical chamber would not propagate through the horizontal tube since they are of the same diameters. However, since limit mixtures exhibit the slowest flame speeds, propagation through the horizontal tube will not be necessary for detection, in that case.

The flame detection subsystem selected consists of the Detector Electronics UV Flame Detection System, a timing device with a 24 V DC clutch, and a DC power supply. When the UV sensor detects a specified level of UV radiation, it feeds a signal to the detector electronic package and actuates an instantaneous alarm relay which closes a 24 V DC circuit and starts the timing device. When the UV radiation falls below the specified level, the relay is opened, and the clock stops timing. This subsystem was checked out and performed very satisfactorily despite a slight interaction at times with UV radiation from the igniter spark. A study of this problem showed that a positive flame propagation test produces a timed interval several times greater than that from an igniter spark

"interaction" (i.e., no propagation) and the interaction does not occur at short spark ignition durations (100 milliseconds or less). In addition, the occurrence of flame propagation has also been verified by (1) the production of an audible ignition/venting sound emanating from the combustion chamber, and (2) a rise in chamber skin temperature, measured at a point on the vertical chamber one inch below the horizontal viewing arm.

The gas composition monitoring subsystem used to sample a gas mixture prior to ignition includes two gas hookups to obtain samples for subsequent gas chromatographic (g.c.) analysis. Gas analyses were performed on a Varian Aerograph 200 gas chromatograph modified with a Beckman 1 cc gas sampling loop. Two columns were used with the chromatograph: a 9 ft Molecular Sieve 5A column for the methane analyses, and a 10 ft Poropak Q column for the other gases. In addition, a General Monitors, Model 170 combustible gas monitor, with a Type 180 sensor, typical of commercially available field units, was used to monitor hydrocarbon concentrations.

The gas hookups and the combustible gas monitor sensor are shown in Fig. 7. The original location for sampling, i.e., on the vacuum line leading to the pressure gauge, was changed to assure a more representative sample for analysis of mixtures involving combustible gases of low volatility, than would be obtained at the previously used location. In flammability tests on the CH_4-O_2 and CH_4-O_2-H_2 gas systems, sampling at the original location was sufficient for obtaining a representative sample since either (1) the gases were flowed simultaneously, in the case of CH_4-O_2, through the flame arrester into the chamber, thereby allowing the *mixed* gases to be introduced into the sampling cylinder, or (2) after mixing the gases as above, water vapor was added and all the gases were mixed by raising and lowering a water reservoir attached to the base of the combustion chamber, before sampling.

Prior to the flammability testing, the rotameters for methane, oxygen, and carbon dioxide were calibrated under flow conditions with the respective gases by either producing P-V-T-time data using a known system volume or by direct means using a wet test meter. Strong confirmation of the satisfactory application of both techniques was obtained in the case of the oxygen flowmeter calibration for which both techniques were employed.

Combustion chamber gas pressure (prior to ignition) was determined by a 0-1000 mm Hg Heise gauge shown in Fig. 7, while its temperature was monitored with two Cu-constantan thermocouples in association with a Kaye ice-point reference junction and a Sargent millivolt recorder, shown in Fig. 5. One thermocouple measured the skin temperature at a point on the vertical chamber one inch below the horizontal arm, while the other was lower on the vertical chamber for monitoring the gross temperature in the base region.

The first technique for loading volatile combustible gas mixtures such as methane and oxygen, involved evacuating the system, metering the gases out of the vent line while establishing the desired combustible gas/oxidant ratio as determined by the rotameter settings, and then feeding the gas mixture through the combustion tube until the system pressure reached one atmosphere. At this point, the gas flow was halted, a gas sample was taken for g.c. analysis, and the gas mixture sparked. It was assumed that the in-line flame arrester would provide adequate mixing of the gases. It should be noted, however, that Zabetakis (Ref. 15) has stated, "Industrially, heterogeneous single-phase (gas) . . . flammable mixtures are probably even more important than homogeneous gas mixtures." The methane concentration was determined (1) by flow metering and (2) by analysis of representative samples of the gas mixtures obtained prior to ignition.

The second technique, involved the addition of water vapor to methane-oxygen mixtures that had previously been loaded into the combustion chamber via the first technique. The water vapor (and liquid water) was introduced into the combustion chamber by utilizing a water mixing reservoir connected to the base of the combustion chamber. The gases were then mixed by appropriately raising and lowering the water reservoir.

The third technique used first with the MEK-oxygen system, employed the liquid reservoir for combustible gases of low volatility. This involved evacuating the system and feeding the liquid compound into the holding vessel or reservoir (see Fig. 4). A portion of the liquid was then expanded into the combustion chamber until the desired combustible gas pressure, as determined by the Heise gauge, was reached. Oxygen was next introduced into the chamber up to a total pressure slightly less than atmospheric. The base of the combustion chamber was then heated approximately 25 degrees C above ambient twice per test, using the combustion chamber tape heater, to establish gas convection currents in the chamber for mixing purposes. Natural heat losses were allowed to cool the chamber during each thermal cycle. Each g.c. sampling cylinder was leak checked, using the downstream portion of the vacuum system, and was either already attached directly to the base of the combustion chamber, or was then attached to the base. The third technique, except for minor variations discussed in the subsequent section under Experimental Results, was employed in all the remaining flammability testing.

EXPERIMENTAL RESULTS

The raw numerical data obtained for all mixtures are tabulated in Appendix B. These data consisted of go/no-go type observations and were reduced by a method due to Mullins (Ref. 24), which gives

$$LEL = 1/2\ (C_L + C_G)$$

where C_L = least concentration of fuel in oxidant observed to give a flammable mixture

C_G = greatest concentration of fuel in oxidant observed to give a nonflammable mixture

A flammable mixture is defined (Ref. 22) as "one capable of propagating flame indefinitely away from, and in the absence of, a source of ignition. That is, an ignition source such as an electric spark must be provided initially, but a flammable mixture will continue to propagate the flame even after the spark has been turned off, while a nonflammable one will not."

Results with Methane

The following values of LEL were obtained as a function of spark ignition duration: 5.35 v/o CH_4 in O_2 at 100 milliseconds, and 5.2 v/o CH_4 in O_2 at 500 milliseconds. Since it is known that a multispark ignition of a given gas system lowers the LEL somewhat below that obtained from a single spark combustion experiment (Ref. 30), it is not surprising to see this difference even though both are multispark ignitions. The 500 millisecond spark ignition time was employed when the shorter spark time produced no indications of ignition and propagation in a mixture. There is every reason to believe that the flame propagation that occurred was sustained and was not dependent on the extended spark ignition time,

especially since nonpropagation also occurred in those cases utilizing the longer ignition time, below the lower LEL. The values corroborate previously determined values by other experimenters of 5.1 v/o (Ref. 14) and 5.4 v/o (Ref. 31) CH_4 in O_2 within the estimated experimental error of ± .1 v/o CH_4 and O_2.

With water vapor (Table B2, Appendix B), two tests resulted in partial flame propagations. Strict application of the flammability criteria to these data would have resulted in their being classified as nonflammable; however, to extract as much information from the data as possible, they have been described as exhibiting partial flame propagation. This term appropriately describes the following phenomenological observations that were noted: (1) the upper chamber thermocouple recorded a smaller ΔT than had been the case for positive tests in the past, (2) the usual sound emanating from the combustion chamber was present, and (3) no time was registered on the UV sensor timing device. It should be noted that the flame detection subsystem was checked each time and found operable. The observations thus indicate that flame ignition had occurred but propagation had not extended to the upper reaches of the combustion chamber. The values obtained by g.c. were normalized for zero water vapor to eliminate the dilution effect of the water vapor so that an unbiased determination of the effect of water vapor on the LEL could be made. The actual quantity of water vapor present in the gas mixtures, i.e., the degree of water vapor saturation of the mixtures, is not known precisely and probably varied somewhat from run to run; however, 50% water saturation is not an unreasonable estimate. During the flammability limit testing, both water vapor and liquid were present in the combustion chamber, having been introduced from the water mixing reservoir. Utilizing all of the data and applying Mullins' technique, the following LEL values as a function of spark ignition duration were obtained: 5.25 v/o CH_4 in O_2 at 100 milliseconds, and 5.2 v/o CH_4 in O_2 at 500 milliseconds

with an estimated experimental error of ± 0.1 v/o CH_4 in O_2. The 500 millisecond spark ignition time was employed when the shorter spark time produced no indications of ignition and propagation in a mixture. Comparison of these LEL values with those for dry methane and oxygen shows that water vapor has an apparently minimal effect on the methane-oxygen LEL.

Results with Methyl Ethyl Ketone (MEK)

The following LEL values were obtained as a function of spark ignition duration: 2.0 v/o MEK in O_2 at 100 milliseconds (ms) and 1.9 v/o MEK in O_2 at 500 ms for MEK-oxygen, and 2.25 v/o MEK at 100 ms and 2.05 v/o MEK at 500 ms for MEK-oxygen-water vapor. Experimental error is estimated to be ± 0.1 v/o MEK in O_2. The values appear consistent with previously determined values for MEK in *air* reported by other experimenters, i.e., 1.9 v/o (Ref. 15) and 1.8 v/o (Ref. 14). For the MEK-oxygen-water vapor system the MEK concentration values obtained by gas chromatography were normalized to zero water vapor so that an evaluation of the effect of water vapor on the LEL could be made without the dilution effect of the water vapor affecting the data. As in the case of the previously measured methane-oxygen system, the effect of water vapor on the LEL appears to be quite small.

Since MEK is very soluble in water, the water mixing reservoir was not employed; mixing was achieved, instead, by heating the base of the combustion chamber with a tape heater to establish gas convection currents in the chamber. Water vapor was introduced into the combustion chamber by attaching a stainless steel, valved cylinder, partially filled with distilled water, to one of the vacuum transfer lines, pumping out the inert gases, and then allowing the water vapor to bleed into the chamber up to a vapor pressure of 13 mm Hg, well below the vapor pressure of water at the lowest temperature seen by any part of the vacuum system. The resulting degree of water vapor saturation varied between 46 and 69 percent depending on the temperature at the time of the run. To load the chamber

with a mixture of gases, the least volatile was introduced first, followed by the remaining gases in order of increasing volatility at room temperature, for instance, water vapor followed by MEK and then oxygen. The pressures of the various gases were measured upon addition to obtain preliminary concentration values for each of the loadings.

Results with Paint Thinner

Neither mixtures with oxygen or oxygen plus water vapor were found flammable at room temperature and atmospheric pressure. The paint thinner used is a commercially available mixture of aromatics, naphthenes, and paraffins. Because of its relatively high flash point of 110 F and the fact that Mullins (Ref. 24) had concluded, as had other investigators, that "flash-point test conditions approximate ... those of the weak (lean) flammability limit," it was felt that the mixture's vapor pressure would probably be insufficient at room temperature to produce a flammable mixture. Nevertheless, LEL measurements using the flammability test apparatus were deemed appropriate since, it is also stated in Ref. 24 that, "It is necessary to stress that, in fact, the flash-point apparatus does not rate the ease of flammability of liquid fuels under all experimental conditions. The further that any given conditions be removed from the conditions of the laboratory flash-point apparatus, the poorer is the flash-point likely to be a measure of ease of flammability."

Experimentally, a sample of paint thinner was loaded into the low-volatility liquid reservoir and vapor from the reservoir, representative of the vapor from a large spill, was bled into the combustion chamber up to its equilibrium vapor pressure. Tests were conducted on four individual gas mixtures, two without water vapor and two with water vapor. The gases were loaded into the chamber in order of increasing volatility at room temperature, and were mixed by the establishment of thermal convection currents in the chamber. The concentrations of paint thinner, deter-

mined by P-V-T measurements, varied from .2 to .3 v/o of the gas mixture. Testing of each gas mixture involved four separate ignition attempts, one for 100 ms and three for 500 ms duration; all proved to be negative in propagating a flame front.

Results with Gasoline

Gasolines are blends that contain a wide variety of hydrocarbons and additives. Accordingly, their flammability characteristics are governed by the method used to extract a vapor sample as well as by the history of the liquid. For example, since the lower or lean limit of flammability, expressed in volume percent, is inversely proportional to the molecular weight of the combustible vapor as noted in Ref. 15, the first vapors to come from a blend, such as gasoline, give a higher LEL value than the completely vaporized sample. Since all of the gasoline-oxygen and gasoline-oxygen-water vapor flammability tests were conducted with samples of gasoline vapor that were withdrawn from the vapor phase of a single liquid gasoline sample, the LEL value of the gasoline should fall as vapor is withdrawn.

The following LEL values, listed in the chronological order in which each respective set of data was measured, were obtained: 1.7 v/o gasoline in O_2, gasoline-oxygen; 1.15 v/o gasoline in O_2, gasoline-oxygen-water vapor; and 1.15 v/o gasoline in O_2, gasoline-oxygen, with an estimated experimental error of ± 0.1 v/o gasoline in O_2. The drop in the gasoline-oxygen LEL with time, i.e., increased number of vapor loadings, confirms the earlier statements regarding fuel blend LEL's. As volatile constituents continue to come off, there is a tendency for the increasing fuel vapor concentration to be coupled with a lowering of the LEL. This means that an initially lean non-flammable mixture might change to a flammable one.

Further verification of the change in gasoline composition as vapor samples are withdrawn was obtained from the g.c. analysis. Essentially all of the constituents of the gasoline vapor exited the g.c. column in the first ten minutes after injection, with the formation of three g.c. peaks. A comparison of these three peaks with those formed when the same measured amount of gasoline vapor is injected from a fresh sample of liquid gasoline into the g.c. shows that the first peak is decreasing, the second remaining about the same, and the third increasing in size as more vapor is withdrawn from the original liquid gasoline sample. If it can be assumed that the most volatile components are present in the first peak and the least volatile in the last peak, then it would appear that later samples of vapor contain proportionally more higher molecular weight species, as time goes on, than the original gasoline vapor. This would result in a lowering of the LEL, as was observed. Also, it should be noted that only the second of the three peaks was used in the g.c. analysis for the determination of gasoline vapor concentration in the gas mixtures.

No correlation of LEL with spark ignition duration could be made since the 500 millisecond (ms) spark ignition time is employed only when the shorter spark time, 100 ms, produces no indications of ignition and propagation, and no 500 ms test gave a positive flame propagation. For the gasoline-oxygen-water vapor system, the gasoline concentration values, obtained by g.c., were normalized to zero water vapor so that an evaluation of the effect of water vapor on the LEL could be made without the dilution effect of the water vapor affecting the data. The effect of water vapor on the gasoline-oxygen LEL appears to be nonexistent.

Experimentally, mixing was achieved by heating the base of the combustion chamber with a tape heater to establish gas convection currents in the chamber. The water mixing reservoir was not employed because samples for g.c. analysis were withdrawn at the base of the combustion chamber, essentially precluding the use of the water mixing reservoir. Confirmation of the truly representative nature of the sampling technique and the adequacy of the mixing was established by a special set of triplicate

samplings of a gasoline-oxygen mixture, the analysis of which by gas chromatograph resulted in the same concentration value of gasoline vapor reported for each sampling. A valved, stainless steel cylinder was used as the gasoline reservoir, rather than the low volatility liquid reservoir, because the former could be easily removed from the flammability apparatus for use by the analytical personnel in their calibrations of the gas chromatograph. In the cases where water vapor was desired in the gas mixture, it was introduced into the combustion chamber by attaching a valved, stainless steel cylinder, partially filled with distilled water, to one of the vacuum transfer lines, pumping out the inert gases, and then allowing the water vapor to bleed into the chamber up to a vapor pressure of 13 mm Hg. The resulting degree of water vapor saturation varied between 55 and 62 percent depending on the temperature at the time of the run. The gases were loaded into the chamber in order of increasing volatility at room temperature, for instance, water vapor followed by gasoline vapor and then oxygen.

CONCLUSION

For the average conditions of 25 C temperature and 730 mm Hg pressure, LEL values were measured for an energy input of 90 millijoules per spark, with a pulse duration of 30 microseconds per spark and a spark rate of 57 sparks per second. Table 6 is a summary of all results - for methane, methyl ethyl ketone (MEK), paint thinner and gasoline - both in dry oxygen and in an oxygen-water vapor mixture. Replication of present data and agreement with other methane-oxygen data (Ref. 14, 31) indicated that the apparatus was yielding valid results for both pure substances and blends. MEK limits in oxygen were about 5% higher than limits in air found by others (Ref. 14, 15). Paint thinner with a distillation range of 312-390 F did not ignite from the lean side under any conditions. A single sample of gasoline with a distillation range of 95-385 F did ignite, and exhibited a decrease in LEL with time, evidence of continuing vaporization of volatiles. The effect of water vapor in amounts

Table 6. SUMMARY OF EXPERIMENTAL LEL DETERMINATIONS

SUBSTANCE	SPARK IGNITION DURATION MILLISECOND	OXYGEN	OXYGEN PLUS WATER VAPOR	OTHER LEL DATA IN: OXYGEN	AIR	REF.
Methane	100	5.35	5.25			
	500	5.2	5.2			
				5.1		14
				5.4±0.1		31
Methyl Ethyl Ketone	100	2.0	2.25			
	500	1.9	2.05			
					1.9	15
					1.8	14
Paint Thinner, AMSCO 20-H	100	No ign	No ign			
	500	No ign	No ign			
Gasoline, Load Led	*A	1.7				
	B		1.5			
	C	1.15				
					1.3	15
				(AvGas, 115/145)		

*A, B, C in chronological order
No spark duration effect

approaching saturation was not significant for methane, paint thinner or gasoline; it did increase LEL's for MEK by about 10%. An increase of spark ignition duration from 100 to 500 milliseconds reduced LEL's by absolute volume percentages in the 0.05 to 0.20 range for the pure substances (methane and MEK), but had no effect on the distillates (paint thinner and gasoline).

OXYGEN AERATION SYSTEMS

A review of the status, as of October 1973, of municipal wastewater treatment plants utilizing oxygen aeration activated sludge reactors, is given in Ref. 8. Table 7, taken from Ref. 8, lists 42 plants in design, construction or operation, with a total designed flow of 7.98 million m^3/day (2109 million gal/day). During the month of October 1974 the 5 plants (Nos. 1, 24, 31, 37, 41) listed in Table 7 as operating or being started up, plus 4 pilot plants were visited for the purpose of obtaining information on the current status of safety in operating plants. During the same period visits were also made to the four principal oxygen aeration process developers (Airco, Air Products & Chemicals, FMC, and Union Carbide-Linde Division), to the Compressed Gas Association, and to the A&E firm (Alexander Potter Associates) designing the Baltimore Plant (No. 11 in Table 7).

A questionnaire shown in full in Appendix A was designed for the plant visits to ascertain data on the total system of safety interest, as diagrammed on Fig. 1. Cooperation by plant personnel was good throughout. The principal data obtained are shown in Tables 8 through 13, as follows:

Table 8	Abbreviations and Metric Conversion Factors for Tables 9 through 13
Table 9	Influent and Primary Data for Oxygen Plants
Table 10	Oxygen Aeration Reactor Data for Oxygen Plants
Table 11	Oxygen Aeration Performance Data
Table 12	Oxygen Aeration Sensors
Table 13	Oxygen Supply Data for Oxygen Plants

Table 9 shows that only plants 1 and 2 (Detroit and Brooklyn) have appreciable amounts of industrial wastes to be treated, and that the strength of the sewage is variable. Combined sewer systems (plants 1, 2, 4, 5) tend to dilute the sewage, and this has the consequence that the oxygen usage, in tons oxygen per million gallon, is lower if other performance variables (such as mixed liquor volatile suspended solids, MLVSS) are constant. In all cases except one the primary sedimentation tanks are

Table 7. MUNICIPAL WASTEWATER TREATMENT PLANTS UTILIZING OXYGEN (Ref. 8)

Plant (1 mgd = 3785 m^3/day)	Design Flow (mgd)	Type of Dissolution System	Status (Oct. 1973)
1. Detroit, Mich.	300	Submerged Turbine	Startup
2. Philadelphia, Pa. (Southwest)	210	Surface Aerator	Design
3. Philadelphia, Pa. (Northeast)	150	Surface Aerator	Design
4. New Orleans, La.	122	Surface Aerator	Const.
5. Middlesex County, N.J.	120	Submerged Turbine	Design
6. Oakland, Calif. (East Bay M.U.D.)	120	Submerged Turbine	Design
7. Dade County, Fla.	120	Surface Aerator	Design
8. Louisville, Ky.	105	Submerged Turbine	Const.
9. Wyandotte, Mich.	100	Submerged Turbine	Const.
10. Denver, Colo.	97	Surface Aerator	Design
11. Baltimore, Md.	73	Surface Aerator	Design
12. Tampa, Fla. [a]	60	Surface Aerator	Design
13. Miami, Fla.	55	Surface Aerator	Design
14. Duluth, Minn.	42	Surface Aerator	Design
15. Hollywood, Fla.	36	Surface Aerator	Design
16. Cedar Rapids, Iowa	32.9	Surface Aerator	Design
17. Harrisburg, Pa.	31	Surface Aerator	Design
18. Springfield, Mo.	30	Surface Aerator	Design
19. Salem, Ore.	26.5	Surface Aerator	Design
20. Danville, Va.	24	Surface Aerator	Const.
21. Euclid, Ohio	22	Surface Aerator	Design
22. Ft. Lauderdale, Fla.	22	Surface Aerator	Design
23. Littleton/Englewood, Colo.	20	Surface Aerator	Design
24. New York, N.Y. (Newtown Creek)	20	Submerged Turbine	Oper.
25. Decatur, Ill.	17.7	Surface Aerator	Const.

[a]Two-stage oxygenation system.

(CONTINUED)

Table 7. (Concluded)

Plant (1 mgd = 3785 m_3/day)	Design Flow (mgd)	Type of Dissolution System	Status (Oct. 1973)
26. Fayetteville, N.C.	16	Surface Aerator	Const.
27. Chicopee, Mass.	15	Surface Aerator	Design
28. New Rochelle, N.Y.	14	Submerged Turbine	Design
29. Muscatine, Iowa	13	Surface Aerator	Const.
30. Winnipeg, Manitoba	12	Surface Aerator	Const.
31. Fairfax County, Va.	12	Surface Aerator	Oper.
32. Jacksonville, Fla.	10	Surface Aerator	Design
33. Brunswick, Ga.	10	Surface Aerator	Const.
34. Tauton, Mass.	8.4	Surface Aerator	Design
35. Morgantown, N.C.	8	Surface Aerator	Const.
36. Lebanon, Pa.	8	Surface Aerator	Design
37. Speedway, Ind.	7.5	Surface Aerator	Oper.
38. Deer Park, Tex.	6	Surface Aerator	Const.
39. Louisville, Tex.	6	Surface Aerator	Const.
40. Mahoning County, Ohio	4	Surface Aerator	Design
41. Calabasas, Calif. (Las Virgenes M.W.D.)	1.8	Converted Air Diffusers	Oper.
42. Cincinnati, Ohio [b]	1.2	Surface Aerator	Design
	2109		

[b]Treatment of Zimpro supernatant.

TABLE 8. ABBREVIATIONS AND METRIC CONVERSION FACTORS FOR TABLES 9 THROUGH 13

Abbreviations

AGC	aerated grit chamber
atm	atmosphere
auto	automatic
avg	average
BOD (5)	5-day biochemical oxygen demand, mg/l
cap	capacity
cfm	cubic feet per minute
comb	combined
cont	continuous
cryo	cryogenic
detent	detention
dia	diameter
dist	distance
DO	dissolved oxygen
equiv	equivalent
FAD	fixed active (fine bubble) diffuser
FB	freeboard
FBS	fine bubble sparger
ft	foot
hr	hour
HSS	hollow shaft sparger
H_2O	water
in.	inch
ind	industrial
injn	injection
LEL	lower explosion (flammability) limit
liq	liquid
mg/l	milligram per liter
ML	mixed liquor
MLSS	mixed liquid (total) suspended solids

TABLE 8. (Concluded)

MLVSS	mixed liquor volatile suspended solids
mol	molecular
NA	not applicable
No.	number
opr	operator
org	organic
O_2	oxygen
PECh	primary effluent channel
ppm	parts per million
press	pressure
psig	pounds per square inch gage
pt	point
recirc	recirculation
res	residential
SA	surface aeration
selec	selectively
shutdn	shutdown
Slr Hse	slaughterhouse
ss	suspended solids, mg/l
ST	surface turbine
St	stage
surf	surface
vac	vacuum
w/	with

Metric Conversion Factors

1 cubic ft per minute	1.69902 m^3/hour
1 foot	0.3048 meter
1 U.S. gallon	0.003785 m^3
1 million U.S. gallons per day	3785 m^3/day
1 U.S. horsepower	1.012 metric horsepower
1 inch of water	248.84 pascal
1 mile	1609 meters
1 U.S. ton	1.016 metric ton

TABLE 9. INFLUENT AND PRIMARY DATA FOR OXYGEN PLANTS

Plant No.	Name and Location	Avg(Peak) 10^6 gal/day Influent	Raw Water % Res.	Raw Water % Ind.	Ind. Waste Type
1.	Detroit Metro, Detroit, MI (new construction)	300	50	50	Varied Organic and Inorganic
2.	Newtown Creek, Brooklyn, NY (was air)	21	60	40	Brewery Plating Slr.Hse.
3.	Westgate, Fairfax Cty., VA (new construction)	12.5 (16.5)	98	2	Plating Solvents Grease
4.	Speedway Indianapolis, IN (new construction)	4.4	75	25	Organic
5.	Blue Plains Washington, DC (EPA-DC Pilot Plant)	0.05	100	0	None
6.	Tapia, Calabasas, CA (was air)	2.0	90	10	Organic
7.	Metro Denver, #1, Commerce City, CO (Pilot Plant)	0.5	75	25	Metallic Slr. Hse.
8.	Englewood, CO (Pilot Plant)	0.05 (0.15)	95	5	Plating Grease
9.	Mountainview, Wayne, NJ (Pilot Plant)	1.0	100	0	-

TABLE 9. (Concluded)

Collection System		Raw:	Primary Sedimentation			
Sewer Type	Detention time, hr	BOD(5) / SS	Tank Type	Detention time, hr	PECh Aeration	In-plant Re-treat
Combined	8-12	100/250	Covered & open	1.0	No	Yes
Combined	"few"	200/184	None	-	No (but AGC)	-
Separate	4,avg	180/205-500	Open	0.25	No	Yes
Combined	0.5	90/150	Open	2.0	No	Yes
Combined	6-8	100/100	Open	0.75	No	Yes
Separate	6,avg	375/350	Covered	0.75	Yes	No
Separate	1/2-4	250/250	Open	1.0	No (but AGC)	Yes
Primary	Effluent	140-210/85-200	Open	1.5-2.0	No	Yes
Separate	1.5,avg	50-180/100-200	Open	2.0	No	Yes

Table 10. OXYGEN AERATION REACTOR DATA FOR O_2 PLANTS

Plant No.	Tank for O_2? ex-air?	Tank Type, No. Stages	Depth+FB(ft), Width (ft), Length (ft)	O_2 Entry & Press, in.H_2O
1 Detroit	for O_2	Closed, 5 stage	30+4, 132, 662	Freeboard Stage 1, 1.5
2 Brooklyn	ex-air	Closed, 4 stage	15+3, 55, 200	Freeboard Stage 1, 1-2
3 Fairfax	ex-air	Closed (St 1-3) Open (St 4)	12, 41, 180	Freeboard Stage 1, 2-3
4 Speedway	for O_2	Closed, 4 stage	16, 44, 88	Freeboard Stage 1, 1.0
5 EPA-DC	for O_2	Closed, 4 stage	14, 5, 20	Freeboard Stage 1, 1-4
6 Tapia	ex-air	Closed, Single stage	15, 30, 116x54	(Freeboard Press $\geq$ 2.5)
7 Denver	for O_2	Open	12+1.5, 10, 40	-
8 Englewood	for O_2	Open, 3 stage	12, 4, 8	-
9 Wayne	ex-air	Open, 2 modules in series	12, 18, 33	To vapor space in module via 1 in. pipe at up to 3 psig

TABLE 10. (Concluded)

O_2 Injection		Rotary Mixers				Gas Compressors		
Depth, ft	Type	Depth, ft	Type	No. Units	Unit HP	For	No. Units	Unit HP
29	HSS	28	ST	8 12	@ 125, @ 75	O_2 Injn	3 3	@ 400 @ 250
14	HSS	13	ST	2 6	@ 50 @ 30	O_2 Injn	5 (all st. + 1 standby)	@ 40
0	SA	0,8	SA, ST	36	@ 55			-
0	SA	0,12	SA,ST	8	@ 7.5			-
12	HSS	11	ST	4		O_2 Injn	12	@ 0.5
15 (40 ft long)	FBS	Mixing from recirc. gas thru conventional air diffusers				Gas re-circula-tion	1 (1800 cfm)	
11	FAD	------				O_2 injn (to 30 psig)	1	@ 7.5
11	FAD	------				O_2 injn (to 30 psig)	1	
		One mixed liquor pump in module						

Table 11. OXYGEN AERATION PERFORMANCE DATA

Plant No.	MLVSS / MLSS, both 10^3 mg/l	Detention time, hr	Oxygen % in gas space		Tons O_2 per 10^6 gal
			Entry	Vent	
1 Detroit	3 / 5	1.8	100	45	0.5
2 Brooklyn	2.4 / 5.0	1.0	90+	35	0.65
3 Fairfax	3 / 4	1.5	100	45	0.5
4 Speedway	6-9	1.8-2.1	91-93	45	0.88
5 EPA-DC	2-8 / 3-10	1.3-2.0	65-90	30-60	0.9
6 Tapia	4	3.6	50	50	0.4-1.1
7 Denver	4	1-3	NA	21	1.0
8 Englewood	3-6	1-2	NA	21	1.0
9 Wayne	2-4 / 2.5-5	1.5-3	40-70	21	.2-.4

TABLE 11. (Concluded)

Auto. Process Control	Relief Valves			Gas Vent		
		In. H_2O set:			Dia.	
	Stages	Press.	Vac.	Where	In.	Dia.
DO in ML	1 thru 4	6	4	St. 5	12	Atm
	5	5	-			
FB Press. (DO, too)	1 thru 3	6	4	St. 4		Atm.
	4	5	-			
FB Press.	1 thru 4	6	6	St. 3 (4 places)		Atm
FB Press. (manual: DO)	1 thru 4	5	3	St. 4	4	Atm
FB Press.	1 thru 4	5	5	St. 4	0.75	Atm
O_2% in Freeboard	-	2	-	tent	2	Atm
DO in ML	NONE				NONE	
DO in ML	NONE				NONE	
DO in Module #1 (manual: press.)	Relief dip tube	6	-	Dip tube bubbler	2.5	Atm

TABLE 12. OXYGEN AERATION SENSORS

Plant No.	DO Sensing: How Often?	DO Sensing: Depth, ft	Alarm	Gas O_2 Sensors: Oxygen Supply	Gas O_2 Sensors: Where
1 Detroit	Cont.	5	-	Cryo Plant	(1) St. 1 & 5 (2) Vent
2 Brooklyn	Grab, twice daily	2 (all st.)	*<85% O_2 (Shutdn if <80% O_2)	*Mol. Sieve Plant	(1) All st. (selec) (2) Vent
3 Fairfax	Grab every 4 hrs	2 (16 pts., all st.)			
4 Speedway	Grab every 4 hrs	2	*<80% O_2 auto. shutdn	*Mol. Sieve Plant	Vent
5 EPA-DC	Grab every 4 hrs	3-5 (4 pts., 1 per st.)	None		All stages
6 Tapia	Cont.	(3 places)	<50% O_2 (manual shutdn)	None	Under tent
7 Denver	*Cont.	4	*If DO <1 or DO >6		atm above ML surf
8 Englewood	*Cont.	*4 (3 places)	*If DO <1 or DO >5 (ppm)		atm above ML surf
9 Wayne	Cont.	1/2-1 (2 places)			atm above ML surf

TABLE 12. (Concluded)

Locations	Combustible Hydrocarbon Sensors		
	LEL Gas	25% LEL Action	50% LEL Action
St. 1 & 5	C_6H_{14}	(1) O_2 purge (2) Vent opens (3) Alarm	(1) O_2 purge (2) All motors stop (3) Alarm
(1) St. 1&4 (2&3, too) (2) Screen		(1) O_2 stops (2) Air purge (3) Alarm	(1) Compressors stop (not mixers) (2) Air purge
St. 1, 3, 4 (4 places)		(1) Alarm (2) Opr. checks influent	(1) Shutoff O_2 (2) Open vents (3) Purge w/air
St. 1 & 4 (2 & 3, too)		(1) O_2 stops (2) Air purge (3) Alarm	(1) O_2 stops (2) Mixers stop (3) Air purge
N O N E			
N O N E			
N O N E			
N O N E			
N O N E			

Table 13. OXYGEN SUPPLY DATA FOR O_2 PLANTS

	On-Site Generation			Oxygen usage, ton/day
	Type plant	Cap., ton/day	Dist., ft from reactor	
1 Detroit	Cryo	180	30	140-180
2 Brooklyn	Mol. Sieve (4 bed)	15	100	11-16
3 Fairfax	-----	--	--	6
4 Speedway	Mol. Sieve (4 bed)	4	30	3.5-3.8
5 EPA-DC	-----	--	--	.045
6 Tapia	-----	--	--	1-2
7 Denver	-----	--	--	0.5
8 Englewood	-----	--	--	.035
9 Wayne	-----	--	--	.18-.38

TABLE 13. (Concluded)

Liquid Oxygen Storage Information			
Cap., tons	Equiv. days	Dist. of transfer from reactor, ft	Miles to liq. O_2 plant
900	4.5	50-60	on-site
53	3-4	25	50
8	1.25	80	20
4	1.0	30	170
9	20	15	15
20	15	30	40
19	30	250	10
1	30	10	10
14	30	12	120

open and retreatment of various plant streams (e.g., filtrate from vacuum filter, filter wash water, sludge thickener supernatant, etc.) occurs. In two cases grit chamber aeration is noted, and the one case of a covered primary tank has primary effluent channel aeration.

Table 10 lists the physical dimensions and equipment and oxygen injection information for all plants. The following discussion and figures illustrate the various schemes and show arrangements for specific plants:

1. Closed reactor; multi-stage; initial oxygen entry into freeboard of Stage 1 with subsequent deep submerged injection through spargers by recirculation compressors; submerged turbine type rotary mixers (Fig. 8):

   Detroit - Figures 9 and 10 (from Ref. 32)
   Newtown Creek, Brooklyn - Figure 11 (from Ref. 8)
   EPA-DC Pilot Plant, Blue Plains - Figure 12 (from Ref. 8)

2. Closed reactor; multi-stage; initial oxygen entry into freeboard of Stage 1 with dissolution by surface aeration rotary mixer; co-axial submerged turbine type rotary mixer (Fig. 13):

   Speedway, Indiana - All stages covered
   Westgate Plant, Fairfax County, Virginia - Last stage open - Figure 14

3. Closed reactor; single-stage; oxygen enters through submerged spargers; gas in freeboard recirculated to conventional (air) diffusers; Tapia plant, Las Virgenes MWD, Calabasas, California - Figure 15

4. Open reactor; direct oxygen injection at high pressure (to 30 psig) through submerged fine bubble fixed active diffusers:

   Denver - 1/2 mgd pilot plant
   Englewood, Colorado - 0.05 mgd pilot plant - Figure 16

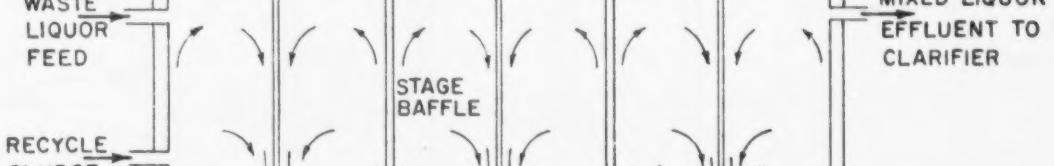

Figure 8. Schematic Diagram of Multistage, Covered-Tank Oxygenation System With Gas Recirculation Compressors and Submerged Turbine/Spargers (from Ref. 8)

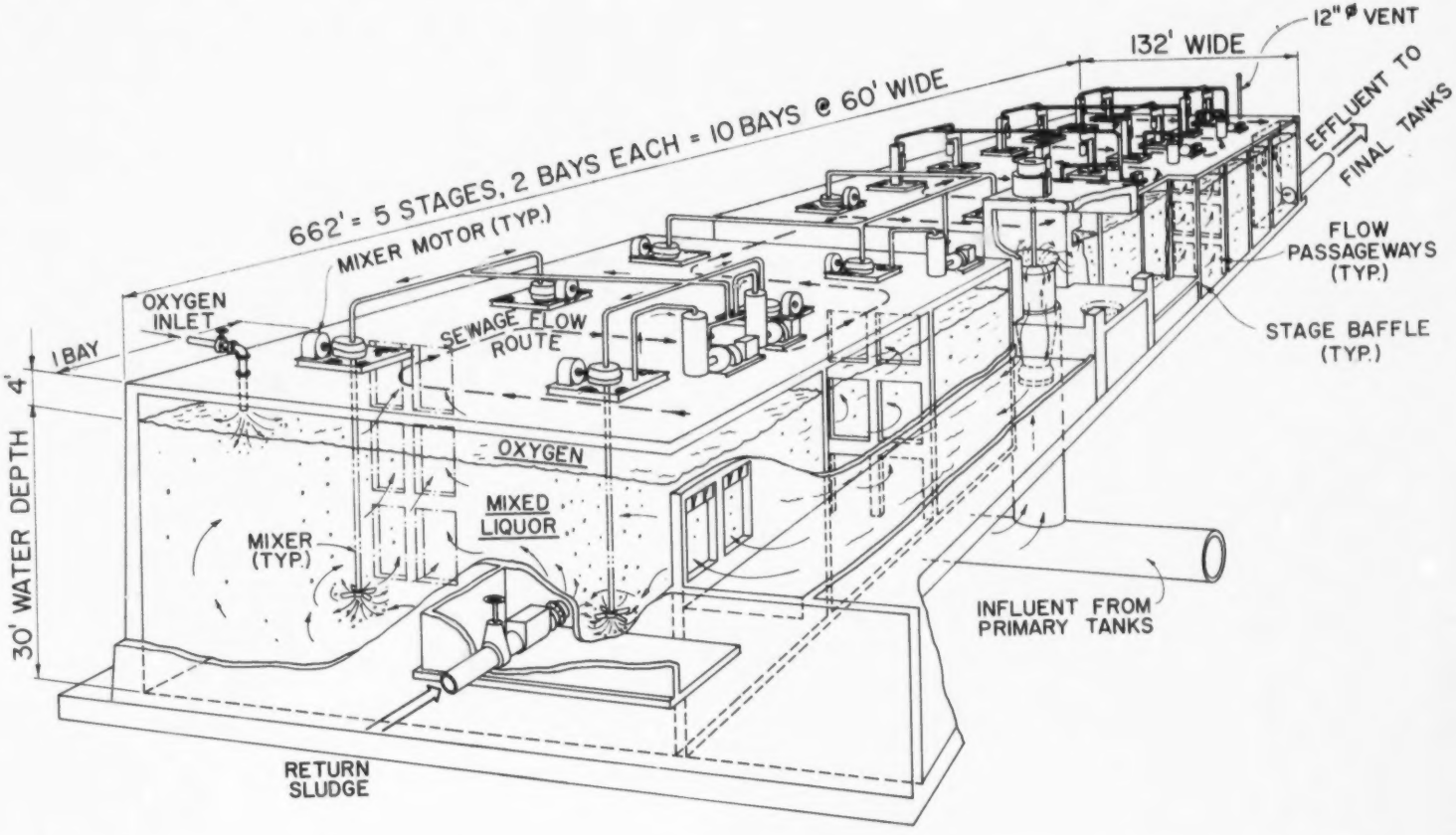

Figure 9. Oxygen Aeration System, Detroit (From Ref. 32)

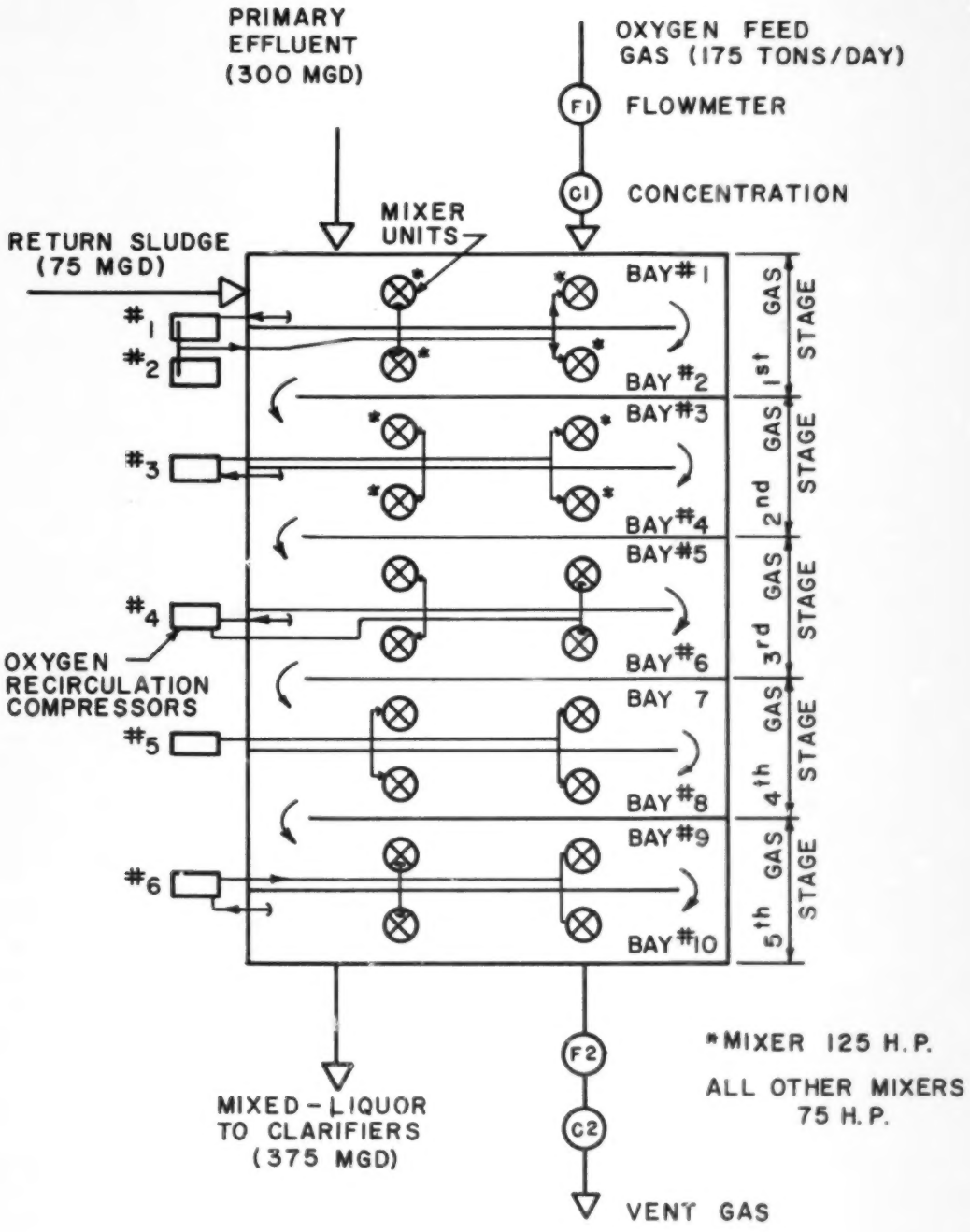

Figure 10. Oxygen Treatment Schematic, Detroit (From Ref. 32)

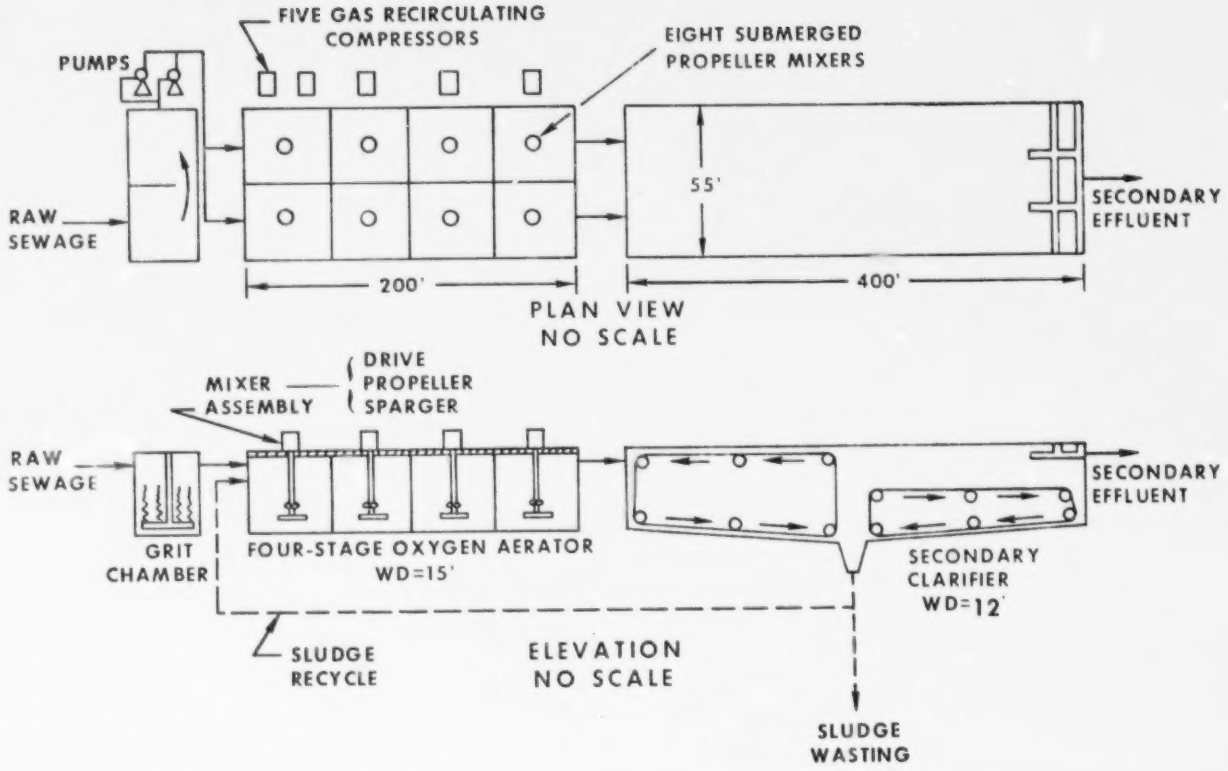

Figure 11. Plan and Elevation Views of Oxygen Aeration Test Bay, Newtown Creek, Brooklyn, New York (From Ref. 8)

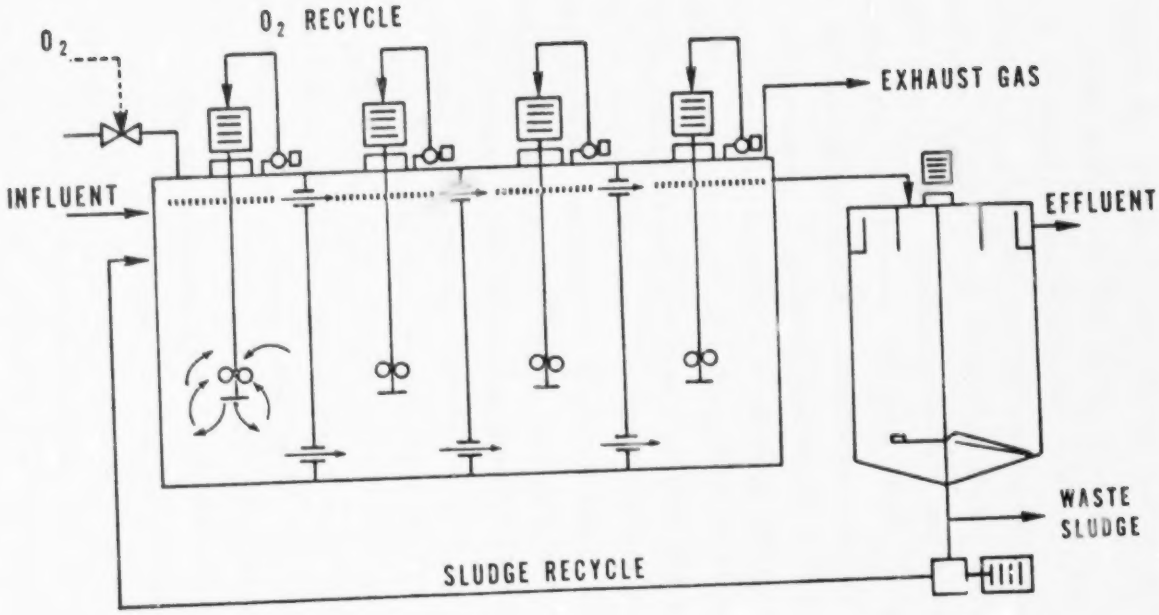

Figure 12. Schematic Diagram of Blue Plains Oxygenation System (EPA-DC Pilot Plant) (Ref. 8)

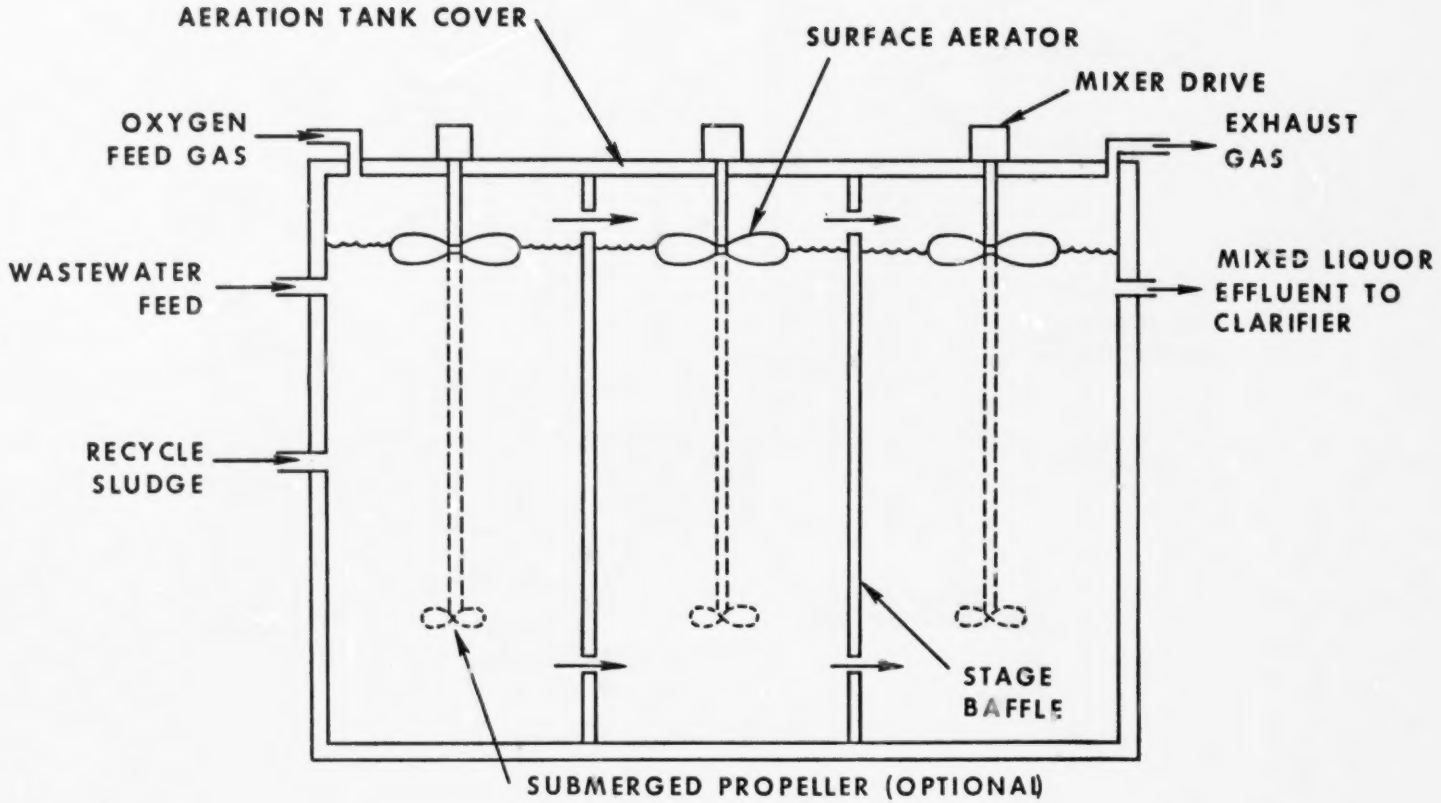

Figure 13. Schematic Diagram of Multistage, Covered-Tank Oxygenation System With Surface Aerators (Ref. 8)

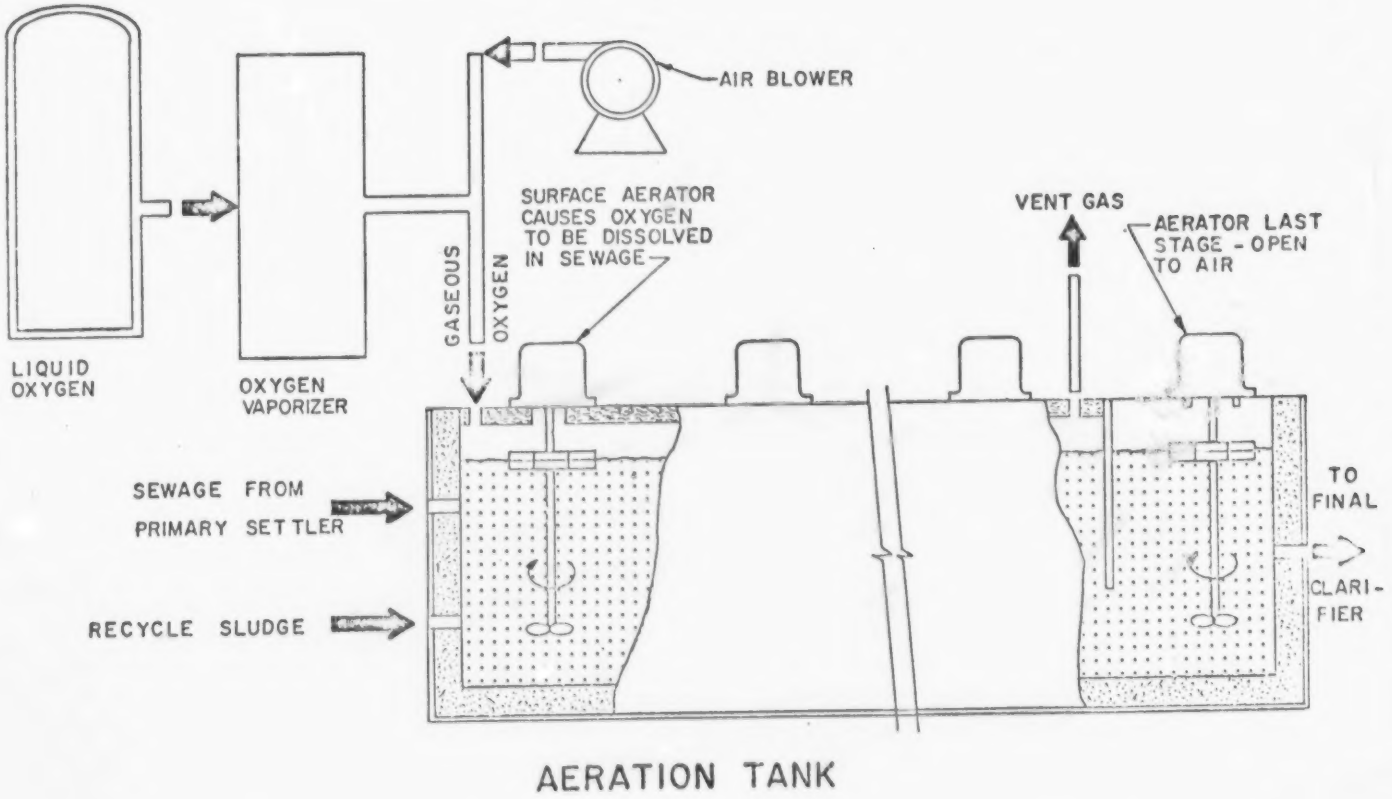

Figure 14. Westgate Oxygen Activated Sludge System, Fairfax County, Virginia (From Ref. 33)

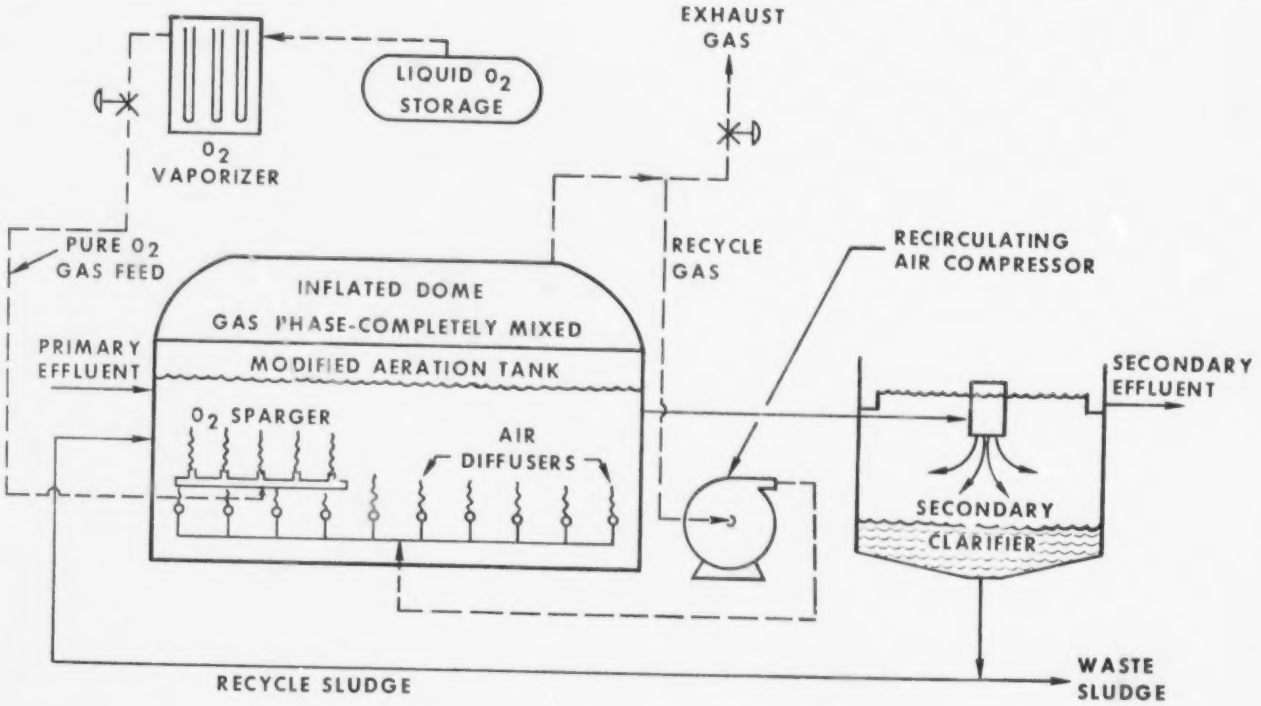

Figure 15. Schematic Diagram of Diffused Air Aeration System Modified to Recirculate Oxygen Gas, Las Virgenes Project, Tapia Plant, Calabasas, California (From Ref. 8)

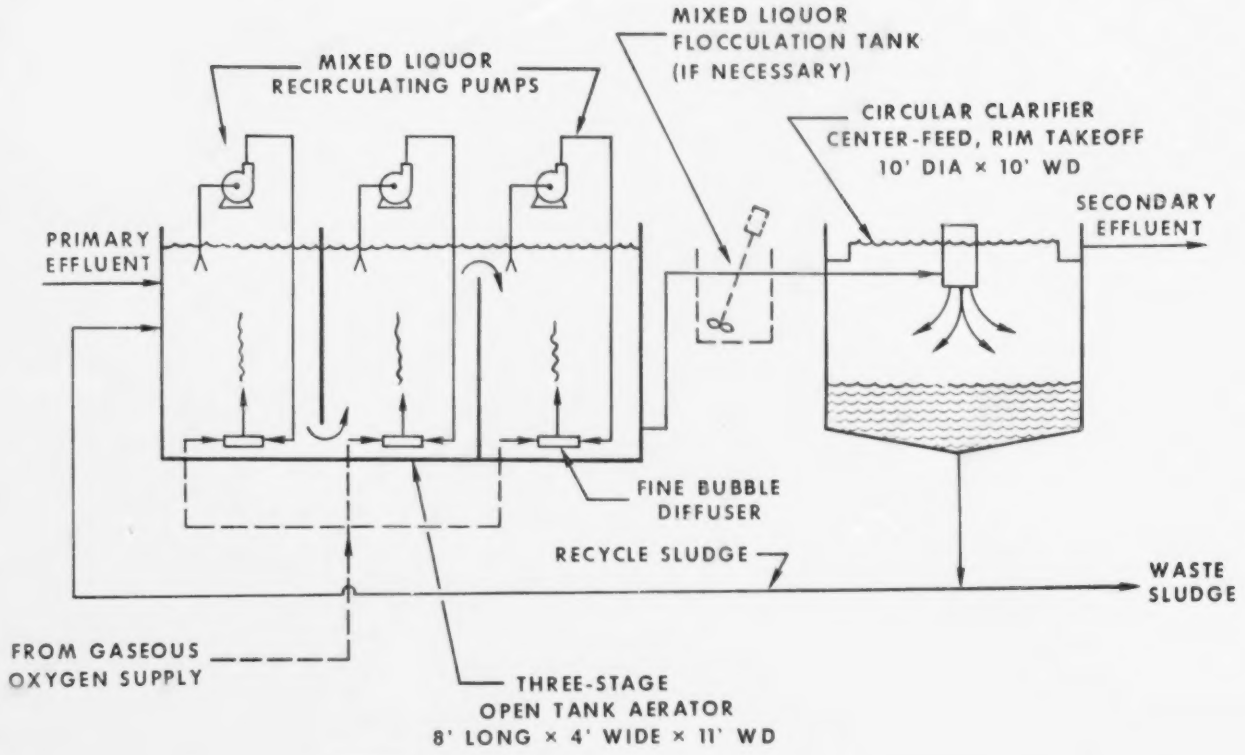

Figure 16. Open-Tank Oxygenation Pilot System, Englewood, Colorado (From Ref. 8)

5. Open reactor; immersed concrete module; oxygen enters module gas space; mixed liquor pumped through module:

   Wayne, New Jersey - Figure 17 (from Ref. 34)

Table 10 shows that the closed reactors include motors to drive mixers and compressors all over the tank in the various stages. The profusion of rotating machinery with potential mechanical and electrical hazards, of course, is not present in the open reactors. Neither is the possibility of structural failure of the top deck of a closed reactor due to over or underpressure in the freeboard. This is the reason for relief valves, as shown in Table 11, set for both overpressure and underpressure (vacuum). The process control is either through DO demand in the mixed liquor (closed and open reactors) or to maintain a given gas pressure in the freeboard (closed reactor). In the latter case a vent at the downstream end of the reactor maintains the pressure profile along the flow direction. With oxygen concentration in the vent gas at 1/2 to 1/3 of the initial high-purity value at entry, over 90% oxygen utilization is achieved.

Table 12 shows the sensors in operating oxygen aeration reactors. None of the plant personnel visited mentioned monitoring hydrogen sulfide in the reactor. The DO was usually sensed in every stage of a closed reactor, principally for process control, but used as an alarmed monitor only in an open reactor (plant 8). With molecular sieve gaseous oxygen generation plants, automatic shutdown (and troubleshooting) procedures were built into the oxygen plant (plants 2 and 4) with provisions to switch over to standby stored liquid oxygen. Otherwise, gaseous oxygen concentrations were sensed in the freeboard and vents of the closed reactors, and above the mixed liquor surface of the open tank reactors.

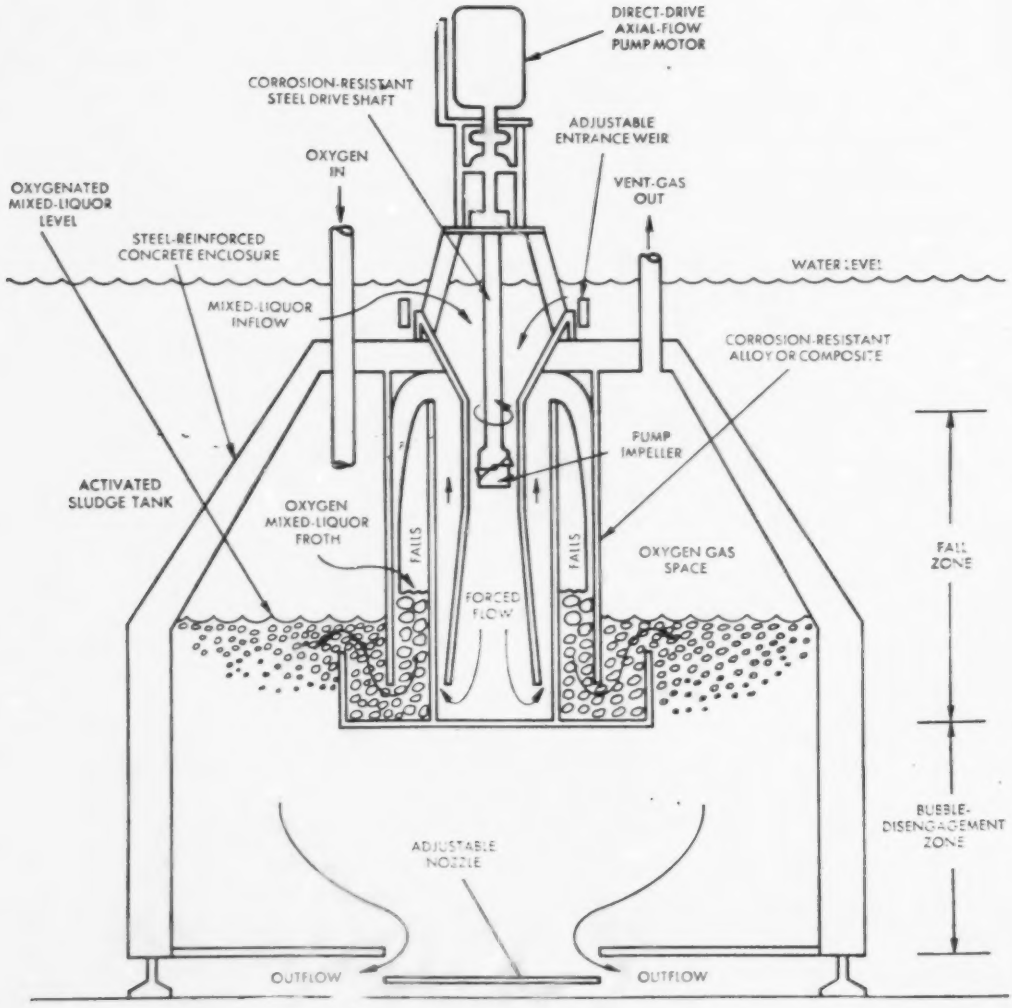

Figure 17. Open-Tank Modular Oxygen Unit, Wayne, New Jersey (From Ref. 34)

The combustible hydrocarbon sensors provided for the largest closed reactor plants (Nos. 1 through 4) all functioned in a similar manner, starting a purge of air or oxygen at 25% LEL, and shutting off all or some of the rotating machinery at 50% LEL. In all plants except one (No. 3) the procedures were automatic at the time of the visits.

Table 13 shows that only one plant had an on-site cryogenic oxygen plant, with two molecular sieve absorbent plants, and the rest (including all the pilot plants) using stored liquid oxygen. The storage capacity permitted operation from a day to a month, in different locations. The oxygen facilities were always in close proximity to the activated sludge reactors.

With the exception of plant 2 which had a hydrocarbon sensor in the headworks (screen) of the treatment plant, no monitoring of potentially hazardous substances in the wastewater upstream of the activated sludge reactor appeared to have been carried out.

While some of the plants had dealt with occasional spills (e.g., solvents) and in one case anaerobic conditions were detected and successfully dealt with by the hydrocarbon alarm system, no major incidents or accidents have been reported.

SAFETY MEASURES AND ECONOMICS

It was made clear in the Approach Section that the total system which must be examined from the standpoint of a preventive safety program includes the wastewater train from collection system to secondary settler, and all on-site oxygen generation and supply equipment as shown in Fig. 1. This figure indicates that hazardous substances may enter the total system from external sources, or they may be produced inside the system by improper operating conditions. Typical of the latter is the formation of hydrogen sulfide and methane in sewers and treatment plant components when the dissolved oxygen level in the wastewater is allowed to drop and anaerobic conditions take hold.

Broadly speaking, the safety program envisaged has strategic and tactical aspects. The safety strategy relies on a variety of rational legal and technical concepts which find expression in controlled actions and behavior, on the part of both the wastewater dischargers (public, industry, etc.) and the sanitation professionals who deal with the discharges. When control is lost, even temporarily, over discharges, operation and maintenance, a tactical situation arises which calls for countermeasures that can be instituted rapidly to avert completely or partially a situation which is potentially dangerous to personnel and plant. The hazards in question may be related to ignition and explosion of combustible materials mixed with oxygen; to toxicity of substances such as hydrogen sulfide; to bodily exposure to extremes of temperature, such as liquid oxygen or fires; and to structural deterioration of plant components due to corrosion from hydrogen sulfide, or to mechanical failure of equipment from a variety of causes.

SAFETY STRATEGY

The safety strategy recommended here is well documented in the companion Safety Manual also prepared on this contract which deals with the total system component by component. The strategy consists of the following major points specifically applied to each piece of equipment (or system):

1. Design (or redesign!) the equipment for efficient functioning under all foreseeable conditions

2. Operate the equipment in an efficient and safe manner - the two go hand in hand - to avoid internal generation of toxic and combustible matter

3. Maintain the equipment adequately to avoid any incipient buildup of conditions conducive to internal generation of toxic and combustible matter. The Safety Manual provides Safety Checklists for all components

4. Control the discharge of toxic and combustible materials into any part of the system, by design, by cooperation of users, and by law

5. Monitor for unsafe concentrations of toxic and combustible matter at critical points in the equipment by use of sensors with alarm features, by frequent testing and analysis, etc.

As an example, here are these five points applied to the collection system:

1. Design the collection system to accepted high standards such that low velocities are avoided, ventilation is provided, etc.

2. Keep the collection system well operated: with adequate flow velocities, ventilated, aerated, chlorinated, as necessary to maintain aerobic conditions to avoid internal generation of hazardous combustible or toxic matter such as hydrogen sulfide and methane.

3. Maintain the collection system by periodic inspections, cleaning, flushing, balling and repair as necessary. Known trouble areas, e.g., where sewer stoppages are likely to occur, should be inspected frequently.

4. Collection system: establish an industrial wastes ordnance which clearly defines the nature and amounts (concentrations) of materials permitted to be discharged to the sewers. Enforce this ordnance to ensure no unknown hazardous materials enter the sewers from the outside. Gather up to date knowledge of all discharges to the collection system, especially from industrial users; know the types of wastes discharged and the periods of peak flow by day and season; and the detention times in the different stretches.

5. Install sensors with audio alarms to monitor oxygen, methane and sulfide at critical points in sewer. Such portable sensors should be used before and during inspection or repair work for personnel protection.

For the case of a covered oxygen aeration activated sludge tank, the strategy would assume the following form:

1. In design ensure that tank materials of construction and structural design features are selected to keep all freeboard walls gastight under required service conditions. The concrete usually chosen for large plants should be of a mix which does not become porous, and the sealant between concrete blocks should keep a tight seal in the face of varying temperature and weather conditions. The top deck which must bear its own weight, as well as that of mixers, motors, compressors, and sometimes vehicular traffic, should be of first class structural design. The metallic moving machinery (aerators, turbines,

spargers, etc.) should be resistant to the corrosive environment and be explosion proof. Access ports, manholes and the like should have tight seals.

The reactor should be equipped with a standby or backup source of oxygen and/or air which can be used in case of a failure of the plant supply, or for purging or leaning out any potentially hazardous mixture which forms in the freeboard. In addition to the usual vent, a pressure relief safety valve should be installed. Further consideration should be given to placing a scrubber in the vent from the relief valve to deal with any combustible or toxic gases which form in the reactor and could endanger the immediate vicinity of the reactor if simply discharged to the atmosphere without treatment.

2. The reactor should be operated such that the design values for dissolved oxygen concentration (DO), and mixed liquor volatile suspended solids (MLVSS) (and other parameters such as F/M ratio) are maintained within allowable ranges. This is to ensure, from a safety standpoint, that (a) anaerobic conditions do not form and generate methane and hydrogen sulfide in the reactor, and (b) the aerobic bacteria population stays alive to perform the biological treatment. There should be a reliable means of oxygen demand and supply.

3. There should be frequent maintenance of the mechanical and electrical components (pumps, compressors, drive motors) to ensure that there are no mechanical failures and that lubrication and cooling are adequate to prevent any overheating of these units. Process and safety sensors (DO, various gas probes in the freeboard, etc.) should be checked for correct functioning. Wall deposits of grease, sulfides, etc., should be periodically removed. All the above apply to the primary influent and return sludge lines, as well as the tank proper. The safety checklist in the Manual gives more details.

4. Since the activated sludge reactor is, so to speak, at the end of the line, control of hazardous substances is limited to avoiding formation of these in the tank by proper operation and maintenance as indicated in paragraphs 2 and 3 above. Upstream events determine what the contents of the primary effluent entering the activated sludge are.

5. Monitoring should be carried out in the mixed liquor and in the atmosphere above it. In the liquor the dissolved oxygen content should be closely monitored; it is likely that a DO probe is also being used for process control. Further, the primary effluent should be analyzed for hazardous soluble matter, such as solvents and inorganic biocidal matter. In the atmosphere above the liquid (freeboard) the concentrations of oxygen, hydrogen sulfide, and methane (and other hydrocarbons) should be monitored. In a large multi-stage tank, multiple sensing probes should be located along the liquid flow direction. It is also useful to know the total pressure in the freeboard; if it exceeds a few inches of water (or other design value) dangerous gases may be building up. Too high or too low a pressure (vacuum) is also dangerous from the standpoint of tank structural integrity. All sensors should be equipped with warning and alarm systems to indicate to the operator when the concentration of a critical substance is about to become dangerously high (except in the case of oxygen when it should not be allowed to become dangerously low).

SAFETY TACTICS

When potentially unsafe conditions arise, obviously something has gone wrong in some part of the safety strategy. What matters then is to obtain speedily factual information on the nature of the hazard - what is the hazardous substance? what is its concentration? where has it been

located? what equipment has failed? and so on. The tactical countermeasures to be taken should be based on the information available, however limited, and they should be carried out without delay. Such tactical measures includes:

1. Early warning of an accidental spill of a hazardous substance into a collection system, or a treatment plant component. Relations between treatment plant personnel and dischargers, including the public, inhabitants of residences, business and industry, should be good enough so that accidental spills are reported by those responsible as soon as the spills occur. Failing this, sensors in the collection system and the headworks of the treatment plant should give warning signals.

2. Chemical or physical treatment to render a hazardous material inert by changing it to a non-hazardous form or other substance. Typical of this are the conversion of toxic hexavalent chromium to non-toxic trivalent chromium by additives; the conversion of hydrogen sulfide to water and elemental sulfur (by adding hydrogen peroxide); and changing the pH of waters harmful to aerobic bacteria to a neutral range. Usually massive doses of additives are needed, but the amount of spilled material to be treated is finite. The treatment can be carried out in the wastewater stream or in holding tanks, see 3. below.

   In this category also falls the addition of air, oxygen or inert gases (nitrogen, carbon dioxide) to potentially flammable mixtures. The effect is to change the mixture to a non-flammable one by leaning it out with oxygen or air, or by adding a diluent which narrows the flammable mixture range (see Fig. 2). This may be accompanied by purging and venting (see 4. below).

3. Process isolation which may be carried out with sufficient early warning, so that in the case of a hazardous spill a sensitive process (like oxygen aeration) may be isolated until safe conditions are restored. All treatment plants are required by the EPA to have dual process units throughout the plant. This permits operation in one or more units while the "off" unit is being inspected, maintained, repaired, or simply on standby. Of particular usefulness are dual or multiple primary sedimentation tanks which can be used as holding tanks to protect the activated sludge tank. It is possible to perform batch type treatment (by additives, skimming off dangerous floatables, aeration, etc.) in such a holding tank to which a spill has been diverted, and later releasing the safe effluent to the activated sludge reactor.

4. Automatic initiation of countermeasures by a sensor or sensors which are linked to one or more process controls. The sensor may act to shut down one type of unit and start up another. An example is given by Baker and Carlson (Ref. 13) with reference to the submerged - turbine UNOX system. Here the freeboard combustible gas detector automatically actuates air blowers to purge the gas space when a combustible concentration of 25% LEL is reached, along with an audible alarm. If the condition is not corrected and the mixture reaches 50% LEL, the purging continues and the recirculation oxygen compressors are shut down. This stops sparging of oxygen into the body of the liquid and reduces mass transfer of any combustibles to the gas space by stripping from the liquid phase. Also, the shutdown of the rotating machinery removes possible spark ignition sources of mechanical or electrical origin.

5. Use of standby and backup equipment in case the hazard is caused by failure or improper functioning of mechanical or electrical equipment. One instance could be the failure of the oxygen supply to the activated sludge reactor. If non-cryogenic oxygen

is generated on-site, a liquid oxygen storage facility supplied by trucks should be on-site for backup. If a cryogenic oxygen generation plant fails, liquid oxygen must be trucked in to keep the liquid oxygen storage tank (which is part of the plant) filled until the plant is repaired. Standby equipment includes (a) air blowers to be used for aeration with air in case all the oxygen supplies fail, and (b) purge air or oxygen blowers activated by alarm systems as mentioned in 4. above. Failure of drive motors, pumps and compressors should be countered by duplicate pumps and compressors with separate drive motors.

For a specific treatment plant and associated collection system, a study should be made of the types of discharges, nature and amounts of possible spills, and detailed characteristics of treatment plant and oxygen supply. With the above classification and the applicable portions of the Safety Manual as guidelines, specific tactical countermeasures should be worked out for the eventualities likely to arise.

SAFETY ECONOMICS

At the start of this study it was thought possible to make a conventional process economic analysis of the safety aspects of oxygen aeration in activated sludge reactors. The incremental cost of safety features was to be established.

During the course of the study several facts became obvious:

- Safety should not be a tradeoff against cost since human lives are involved. The poor record of safety in treatment plants (detailed in the Introduction of this report) before oxygen aeration began indicates that in many plants safety programs have been deficient or lacking. Now that oxygen aeration has brought with it increased hazards, it is the more vital to institute adequate safety measures in plants.

- With very few exceptions the sensors, redundant equipment, process procedures and maintenance requirements in treatment plants are necessary for operational reasons, as well as for safety. This is equivalent to saying that a well-operated plant (i.e., one which puts out a high quality effluent) is a safe plant.

- Existing plants which are converting from air to oxygen aeration in activated sludge reactors, need to add safety features not only in the activated sludge reactor, but also in the remainder of the plant. The extent of these additions depends on what safety features were present in the individual plants.

If these statements are accepted, two things become clear: the capital and O&M costs of safety items are a small fraction of the total plant costs, and the exact amount of these safety costs can only be determined for a new plant in which all safety features are included from scratch.

Reference to the companion Safety Manual reveals that for a properly equipped new plant capital cost items related to safety are primarily detection equipment:

1. Personnel safety equipment: self-contained breathing apparatus, protective clothing, first-aid equipment, etc.

2. Hydrogen sulfide sensors, all-weather, with remote readout and alarm - say, 4 required for headworks, primary and activated sludge reactor

3. Dissolved oxygen sensors, all-weather, with remote readout and alarm - say, 4 required, as for hydrogen sulfide sensors

4. Hydrocarbon sensors, all-weather, with remote readout and alarm - say, 4 required as above

5. Gas phase oxygen analyzer, all-weather, with remote readout and alarm - say, 4 required as above

Now the FOB cost for a typical sensor except that for hydrogen sulfide does not exceed $1,000 (1975 prices), while for hydrogen sulfide that figure lies below $2,000. Doubling these figures to include shipping and installation costs, results in $40,000 to which may be added some $10,000 for first aid equipment for a total of $50,000. This value is applicable to smaller plants of, say, about 10 mgd. For medium (50-100 mgd) and large (100 mgd and up) plants the expenditure will double. Here the fact that certain probes, such as those for dissolved oxygen, are also used for process control is not considered.

The economics of safety features, then, indicate that capital costs even for a small plant would not exceed a few percent of the capital cost of the plant as a whole. A similar statement can be made for O&M costs, considering the small amount of additional manpower and materials needed to operate and maintain the safety sensing equipment. This presupposes that operators have been properly trained in the use and maintenance of the sensing equipment.

The economics of safety in treatment plants with oxygen aeration activated sludge systems may be summed up by saying that safety is essential and that it can be obtained at relatively small expense.

SAFETY MANUAL AND CHECKLISTS

This Section is a guide to the complete "Safety Manual for Wastewater Treatment with Oxygen Aeration" which appears in separate covers as an EPA Report. The preparation of the manual was undertaken when most of the previously presented work was well under way. As pointed out in the Approach, all potential sources of hazardous materials were to be covered, and this included not only the activated sludge reactor, but all the collection system, treatment plant upstream of the activated sludge reactor, and all on-site oxygen generation and storage equipment. In addition, special consideration was given to the subject of industrial wastewater which most large urban treatment plants must handle, and which can create special problems. Part of the manual was also devoted to the organizational side of plant safety which is an essential part of any safety manual. Accordingly, the manual is divided into five chapters:

I. Collection Systems
II. Treatment Systems
III. Treatment of Industrial Wastes
IV. Oxygen System
V. Personnel Safety Requirements

Chapter I is subdivided into major headings dealing with service area identification, waste identification, sewage flow peaks, collection system evaluation and collection system maintenance. The chapter ends with the safety checklist for collection systems.

Chapter II discusses potential hazards, recommended design and operation, monitoring and alarm systems in all treatment plant components of interest: plant influent station with open and enclosed headworks; primary sedimentation in rectangular and circular, open and enclosed tanks; open and enclosed oxygen aeration activated sludge reactors; and return activated sludge systems. Safety checklists are provided for the major treatment plant components.

Chapter III deals with special problems created by industrial wastes in the various plant components, and points out safety approaches to large BOD loadings and potentially biocidal inorganic wastes.

Chapter IV contains sections of general interest, such as properties, hazards and materials compatibility of oxygen; general oxygen production plant considerations; and air and oxygen compressors. Subsequent sections deal with specific oxygen supply systems: molecular sieve absorbent air separation plants, cryogenic air separation plants, and stored liquid oxygen. Safety checklists are provided for oxygen in general, and for the oxygen generation plants and oxygen storage.

Chapter V addresses itself to matters of staffing, training, safety meetings first aid and medical services, and personal safety and fire-fighting equipment.

The compartmentation of the manual permits its revision in any part as more up-to-date information, equipment, or instrumentation become available and are deemed suitable for inclusion in the safety manual.

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APPENDIX A

EPA OXYGEN SAFETY PROJECT 1974

PLANT QUESTIONNAIRE

EPA OXYGEN SAFETY PROJECT 1974

PLANT QUESTIONNAIRE

DATE: _____

NAME OF PLANT _____

LOCATION _____

PERSONNEL: _____ TITLE _____

_____ _____

_____ _____

_____ _____

_____ _____

STATUS

LITERATURE ON PLANT

OPERATING MANUAL _____
SAFETY MANUAL _____
FLOW SCHEMATIC _____
TABLE OF ORGANIZATION _____
TAILGATE SAFETY MTG. _____

WASTEWATER TRAIN

SEWAGE CHARACTERISTICS:

RESIDENTIAL	_____ %
INDUSTRIAL	_____ %
OTHER	_____ %
"	_____ %
	_____
	100%

INFLUENT RATE:

_____ AVG
_____ MAX DAILY
_____ TIME OF YR

SOURCES:

CESSPOOL & SEPTIC TANK?
IF SO, DUMPED IN PLANT _____ OR SEWER _____?
ORGANIC _____
METALLIC _____
REFINERY _____
VOLATILES _____
RESTAURANTS _____
SLAUGHTER HOUSES _____

SEWERS:

COMBINED _____ SEPARATE _____
AVG VELOCITY _____ AVG DETENTION TIME _____
MAINTENANCE EVERY ____ YEARS
SPILL? (OIL, ORGANICS, METALS) _____
ANALYSIS OF RAW SEWAGE _____

HEADWORKS: TYPES & SIZES OF EQUIPMENT

_____

_____

_____

_____

PRIMARY:

COVERED SEDIMENTATION SYSTEM? _____
AVG. PRIMARY DETENTION TIME _____
RAW SLUDGE PUMPING SCHEDULE _____
PRI. EFFLUENT CHANNEL AERATION? _____
IN-PLANT RETREAT? _____
IF SO, DIGESTER SUPERNATANT? _____
WASTE ACTIVATED SLUDGE? _____
SKIMMINGS? _____

AERATION TANK:

USED FOR AIR BEFORE? _____ NEW FOR O_2? _____
AVG. DETENTION TIMES _____
TYPE OF SYSTEM _____
SIZE & THROUGH PUT _____
MLVSS (MG/L): _____
ATM. ANALYSIS: O_2 _____ N_2 _____
CO_2 _____ H_2 _____
VENTING SYSTEM ON AERATION? _____
_____
VENT GAS DISPOSAL? _____
_____
HOW CLOSE TO OTHER TREATMENT UNITS? _____
_____
D.O. SAMPLING: GRAB _____ CONTIN. _____
IF GRAB, HOW OFTEN? _____
D.O. DATA: INLET _____
(LOCATION) _____
(LOCATION) _____
OUTLET _____
TYPE & MAKE OF D.O. SENSOR? _____
_____
_____
H/C SENSORS (TYPE, MAKE, LOCATIONS, ALARM) _____
_____
_____
_____
_____
_____
_____

AERATION TANK (concluded):

OTHER SENSORS? _____

COMPRESSOR DATA (IF APPLICABLE) _____

DIFFUSION EQUIPMENT DATA (TYPE, MATERIALS) _____

ACCESS FOR REPAIR _____

SAFETY PRECAUTIONS (CLOTHING, TOOLS, etc.) _____

OUTLET CONFIGURATION OF AERATION-TANK (MIXED LIQUOR, etc.)

SOLIDS HANDLING (TYPE) _____
IF DIGESTION, AEROBIC? _____ ANAEROBIC? _____
DISTANCE FROM AERATION _____

OXYGEN TRAIN _____ O_2 FLOW SCHEMATIC? _____
O_2 LAYOUT (DIMENSIONED)? _____

ON-SITE GENERATION? _____ IF SO, TYPE (CRYO, PSA) _____
CAPACITY _____
MFR. AND DATE _____
OPERATIONS AND SAFETY INFO. _____
LOCATION (FT. FROM AERATION TANK) _____

OFF SITE? _____ PLANT LOCATION AND DISTANCE _____
TONNAGE USE _____
LOCATION OF TRANSFER _____
SPILL PROTECTION (MOAT, etc.) _____
FEEDRATE _____

VAPORIZATION

CONTROL OF AREA (FENCED, PIPING WRAPPED, etc.) _____

PIPING (MATERIALS, SIZE, LENGTH) _____

CONTROL OF PROCESS (DEMAND?) _____

VALVING (MATERIALS, SIZE, LENGTH) _____

SEALS _____

INSTRUMENTATION _____

CONTROLLERS _____

INJECTION

PRESSURE _____ BUBBLE SIZE _____

LOCATIONS _____

COMPRESSOR (TYPE, CAPACITY, NO. REQ., MATERIALS, HP) _____

OPG & SAFETY & REPAIR MANUALS? _____

CONTROL (D.O., DEMAND, --) _____

IF DEMAND: HYDR. FLOW _____

ORG. LOAD (BOD RESP.) _____

O_2 RECYCLE? _____

LABOR & COST DATA

OPG. INFO & SHIFTS _____

MANPOWER (HEAD → END OF AERATION) _____

TONS O_2 PER 10^6 GAL _____

COST OF O_2 _____ COST PER MG _____

ORGANIZATION & SAFETY

PERSONNEL ASSIGNED TO SAFETY FUNCTIONS

RESPONSIBILITY & CHAIN OF COMMAND

SAFETY EQUIPMENT

FAILURE & ALARM PROCEDURES

OPERATIONAL PROCEDURES

STARTUP O_2 PLANT

STARTUP AERATION SYSTEM

TRANSIENTS

SHUTDOWN AERATION

SHUTDOWN O_2 PLANT

EXPERIENCES WITH O_2 (RUN TIME, DOWNTIME, etc.)

APPENDIX B

RAW DATA FROM FLAMMABILITY TESTS

Table B-1:	Methane - oxygen
Table B-2:	Methane - oxygen - water vapor
Table B-3:	Methyl ethyl ketone - oxygen
Table B-4:	Methyl ethyl ketone - oxygen - water vapor
Table B-5:	Gasoline - oxygen
Table B-6:	Gasoline - oxygen - water vapor

g.c. = Gas Chromatography

Table B-1. Methane-Oxygen Flammability Data

Pressure: 745-760 mm Hg
Temperature: 23-27° C
Energy: 90 millijoules/spark
Pulse Duration: 30 microseconds/spark
Rate: 57 sparks/sec

CH_4 Volume % by Flow Metering,	CH_4/O_2 Volume % by Gas Chromatography*	Spark Ignition Duration, Milli-seconds	Flammable? Yes	No
5.2	5.4/93.4	100		x
5.2	4.4/93.8	100		x
5.2	4.8/94.3	100		x
5.6	5.6/94.0	100	x	
5.4	5.3/94.8	100	x	
5.2	5.0/95.1	100		x
5.3	5.2/94.5	100		x
5.3	5.2/94.5	500	x	
5.2	5.2/95.7	100		x
5.2	5.2/95.7	500		x
5.3	5.2/95.0	100		x
5.3	5.2/95.0	500		x
5.4	5.4/95.2	100		x
5.4	5.4/95.2	500	x	
5.5	5.3/94.7	100		x
5.5	5.3/94.7	500	x	

*Values adopted for calculating Lean Flammability Limit

TABLE B-2

METHANE-OXYGEN-WATER VAPOR FLAMMABILITY DATA

Pressure:	738-747 mm Hg
Temperature:	25-28 C
Energy:	90 millijoules/spark
Pulse Duration:	30 microseconds/spark
Rate:	57 sparks/sec

CH_4 Volume %			Flame Propagation?		
by Flow Metering	by Gas Chromatography*	Spark Ignition Duration, Milli-seconds	Yes	No	Partial
5.6	5.6	100	x		
5.2	5.0	100		x	
5.2	5.0	500		x	
5.4	5.2	100	x		
5.3	5.1	100		x	
5.3	5.1	500			x
5.2	4.9	100		x	
5.2	4.9	500		x	
5.3	5.3	100		x	
5.3	5.3	500			x

*Values normalized for zero water vapor and adopted for calculating the lean flammability limit.

TABLE B-3

METHYL ETHYL KETONE - OXYGEN FLAMMABILITY DATA

Pressure: 715-732 mm Hg
Temperature: 25.5-29.2 C
Energy: 90 millijoules/spark
Pulse duration: 30 microseconds/spark
Rate: 57 sparks/sec

MEK Volume %		Spark Ignition Duration	Flame Propagation?	
by P-V-T	by g.c.*	Milliseconds	Yes	No
2.6	1.9	100		x
2.6	1.9	500	x	
2.4	2.4**	100		x
2.4	2.4**	500		x
2.6	2.2	100	x	
2.5	1.9	100		x
2.5	1.9	500		x
2.4	1.7	100		x
2.4	1.7	500		x
2.6	1.8	100		x
2.6	1.8	500		x
2.7	2.0	100	x	
2.5	1.8	100		x
2.5	1.8	500	x	
2.5	1.8	100		x
2.5	1.8	500	x	
2.4	2.0	100		x
2.4	2.0	500		x

*Values used for calculating the lean flammability limit.

**Anomalous values eliminated on statistical basis.

TABLE B-4

METHYL ETHYL KETONE - OXYGEN-WATER VAPOR FLAMMABILITY DATA

Pressure:	710-714 mm Hg
Temperature:	21.2-28.0 C
Energy:	90 millijoules/spark
Pulse duration:	30 microseconds/spark
Rate:	57 sparks/sec

MEK Volume %		Spark Ignition Duration	Flame Propagation?	
by P-V-T	by g.c.*	Milliseconds	Yes	No
2.5	2.6	100	x	
2.3	2.3	100	x	
2.1	2.4	100	x	
1.8	1.6	100		x
1.8	1.6	500		x
1.9	1.7	100		x
1.9	1.7	500		x
2.0	1.9	100		x
2.0	1.9	500		x
2.1	1.6	100		x
2.1	1.6	500		x
2.3	2.2	100		x
2.3	2.2	500	x	

*Values normalized to zero water vapor and used for calculating the lean flammability limit.

TABLE B-5

GASOLINE-OXYGEN FLAMMABILITY DATA

Pressure:	709-714 mm Hg
Temperature:	20.6-29.2 C
Energy:	90 millijoules/spark
Pulse Duration:	30 microseconds/spark
Rate:	57 sparks/sec

Gasoline Volume %	Spark Ignition Duration	Flame Propagation?	
by g.c.	Milliseconds	Yes	No
1.6	100		X
1.6	500		X
1.9	100	X	
1.7	100	X	
1.7	100		X
1.7	500		X
1.8	100	X	
1.6	100		X
1.6	500		X
1.1*	100		X
1.1*	500		X
1.2*	100	X	
1.1*	100		X
1.1*	500		X

*Flammability tests conducted subsequent to those listed in Table B-6

TABLE B-6

GASOLINE-OXYGEN-WATER VAPOR FLAMMABILITY DATA

Pressure:	710-714 mm Hg
Temperature:	22.7-25.0 C
Energy:	90 millijoules/spark
Pulse Duration:	30 microseconds/spark
Rate:	57 sparks/sec

Gasoline Volume %	Spark Ignition Duration	Flame Propagation?	
by g.c.*	Milliseconds	Yes	No
1.4	100	X	
1.3	100	X	
1.0	100		X
1.0	500		X
1.1	100		X
1.1	500		X
1.4	100	X	
1.2	100	X	

*Values normalized to zero water vapor.